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Otto G. Freyermuth.

A SYSTEM OF INSTRUCTION
IN
QUALITATIVE CHEMICAL ANALYSIS,

BY

ARTHUR H. ELLIOTT, Ph. D.,

Professor of Chemistry and Physics, and Director of the Chemical Laboratory
in the College of Pharmacy of the City of New York.

SECOND EDITION.



1894:

PUBLISHED BY THE AUTHOR.

COLLEGE OF PHARMACY OF
CITY OF NEW YORK.

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1894

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PREFACE TO SECOND EDITION.

The hope expressed in the Preface to the first edition of this little volume, "that the same will be found of service to others," has been fully realized. Owing to the fact that a number of institutions (six) have adopted the volume as a text book for practical instruction, the first edition was exhausted in a little over one year after it left the press.

The present edition is a complete revision of the type, with some additions, and it is believed that as the work becomes better known it will be still further appreciated.

ARTHUR H. ELLIOTT.

NEW YORK, January, 1894.

INTRODUCTION.

It must be distinctly understood that the following pages are written for those who have a laboratory at their disposal, and a teacher at hand who is competent to show the manner of performing the more important experiments. With beginners it will be found necessary to proceed slowly at first in order to make them careful experimenters, and more patience is required at this point than would at first sight seem to be called for.

The course of instruction followed in these pages presupposes that the student has already a knowledge of the fundamental principles of chemistry, or is attending a course of instruction in the same, while he is working at the practical details of chemical analysis. This knowledge need not be very extensive for him to understand most problems in the writing of the more simple of the equations, and in a short time the difficult ones will prove interesting to him and he will work them out without assistance.

No attempt has been made to give instruction in chemical equations or in other theoretical questions. These are left to the judgment of the instructor to interpolate.

The method of making solutions of substances insoluble in water is explained after the student has become acquainted with the methods of analysis. At the beginning all solutions are prepared for him (see Chapter XIV.)

After a few operations involving precipitation, filtering and washing precipitates, it is best to take up at once the separation of the metals into groups; and having shown the student each step of the manipulation, let him repeat it at once, before going on to the next; and above all things he should imitate the instructor. In this last particular the quantity of reagents used is a most important point to insist upon, and well repays the time spent in making the student repeat his work if he fails to imitate the instructor closely.

In order to limit the volume of fluid handled, and at the same time control the quantity of reagents used, all the operations must be performed in test-tubes, small dishes, etc.

In the separation of the metals into groups the student should study this alone without regard to the individual members of the groups themselves: thus, to begin, in the first group one metal only is taken, with one metal of each of the other groups, as, for example, Silver, Copper, Iron and Calcium. After the student has been shown the method of separating these metals into groups, he is made to repeat the operations entirely alone, the instructor giving him another set of metals, such as a Mercurous Salt, Cadmium, Zinc and Barium; thus making him acquainted with the fact that the reagents used give precipitates that vary in color even in the same group.

Above all things the student should work with the instructor, and at exactly the same moment, upon the same materials and with a parallel set of apparatus, thus insuring success and giving a confidence inspired by no other method of working.

The method here described can be readily applied in classes of one hundred if the instructor is on a raised rostrum, where he can be easily seen by every member of the class, and where also he can note the progress of the individual student without difficulty, the rate of advance being determined by the progress of the reasonably bright members, and each step being explained as the work proceeds. Solutions of the metals are studied first; acids and salt radicals are taken up afterwards.

APPARATUS REQUIRED BY EACH STUDENT.

1. Ring-stand with ring, 2 inches inside diameter
- Bunsen burner
- Two feet of $\frac{1}{4}$ inch rubber tubing
- Blowpipe tube for burner
- Blowpipe with fine tip
- Forceps of iron
- Three-inch steel spatula
- Triangular file, 6 inch
- Rat-tail file, 6 inch
- Pipe-stem triangle
- Charcoal from wood, not moulded
- Charcoal borer
- Platinum foil, $2\frac{1}{2}$ by 1 inches

Platinum wire three inches long, in glass holder

Blue glass, 2 by 3 inches

Mortar and pestle, 4 inch

Berlin evaporating dishes, $2\frac{1}{2}$ and 3 inches

Funnels, 2 and 3 inches

Twelve test-tubes, $\frac{5}{8}$ by 6 inches

Test-tube stand of wood

Test-tube brush

Two watch-crystals, 2 inch

Hydrogen sulphide generator; see **10**

Wash-bottle with tubes, 16 oz.

Glass rods, 3 and 4 inches

Filter-papers, 3 and 4 inches

Advanced students may be supplied with the following apparatus in addition to the above:

Small beakers, 100 Cc.

Porcelain crucible, 1 inch

Crucible tongs

Platinum crucible

REAGENTS NEEDED BY EACH STUDENT.

2. These should be supplied to each student in bottles having glass stoppers, except the solution of Potassium Hydroxide, which should have a rubber stopper. The strength of each solution is given in the following list and is made with water unless otherwise stated. The strength of solutions means 1 gramme in cubic centimeters; thus, 1 in 5 means 1 gramme in 5 cubic centimeters.

Hydrochloric Acid (concentrated)

Nitric Acid (concentrated)

Sulphuric Acid (concentrated)

Acetic Acid (U. S. P.)

Ammonium Chloride 1 in 5

Ammonium Hydroxide (1 of Aqua Amm. Fort. and 2 of water)

Ammonium Sulphide; see **3**

Ammonium Carbonate; see **4**

Ammonium Oxalate 1 in 25

Sodium Hydroxide 1 in 5

Potassium Sulphocyanide 1 in 10

Disodium Orthophosphate 1 in 10
 Magnesium Sulphate 1 in 10
 Potassium Dichromate 1 in 20
 Barium Chloride 1 in 10
 Calcium Chloride 1 in 10
 Calcium Hydroxide (Lime Water), saturated
 Milk of Lime (Lime boiled several times with water to free it
 from alkalies)
 Potassium Iodide 1 in 20
 Silver Nitrate 1 in 20
 Potassium Ferrocyanide 1 in 10
 Alcohol (ordinary)
 Carbon Disulphide
 Lead Acetate 1 in 10
 Mercuric Chloride 1 in 20
 Ferric Chloride: Liquor Ferri Chloridi U. S. P. 20 Cc., water
 80 Cc.
 Ammonium Sulphate; see 5
 Sodium Hypochlorite; see 5b
 Cupric Sulphate 1 in 10
 Platinic Chloride 1 in 20
 Molybdic Solution; see 5a
 Nessler's Solution; see 5c

The following reagents are supplied to the student in wide-mouthed bottles :

Sodium Carbonate, anhydrous
 Sodium Nitrate, powdered crystals
 Borax, fused and powdered
 Potassium Ferricyanide, crystals (dissolve as required; solution
 decomposes)
 Iron Sulphide, coarse powder
 Ferrous Sulphate, crystals
 Potassium Chlorate, crystals, small
 Glycerin, concentrated
 Starch
 Copper wire, 1 inch pieces, and sheet zinc, $\frac{1}{2}$ by $\frac{1}{2}$ inch pieces
 Litmus Paper, red and blue.

3. *Ammonium Sulphide* should be made by saturating Ammonium hydroxide (1 of Aqua Amm. Fort. and 2 of water) with Hydrogen Sulphide, and then adding an equal volume of the same Ammonium Hydroxide.

4. *Ammonium Carbonate* is made by taking

Ammonium Carbonate (clear lumps)..... 17 Gm.

Ammonium Hydroxide (1 Aqua Amm. Fort.,
5 water)..... 30 Cc.

Water to 100 Cc.

and shaking the mixture in a bottle until the lumps are dissolved.

5. *Ammonium Sulphate* is made by taking

Sulphuric Acid (concentrated) 10 Cc.

Water 40 Cc.

and adding excess of Ammonium Hydroxide to the mixture, or it may be made as needed.

5a. *Molybdic Solution* is made as follows :

Take

Molybdic Acid..... 5 Gm.

Ammonium Hydroxide (1 of Aqua Amm. Fort.,
2 of water)..... 20 Cc.

Nitric Acid (1 of concentrated, 1 of water).... 80 Cc.

Dissolve the Molybdic Acid in the Ammonium Hydroxide with gentle warming. Pour the solution thus obtained into the acid, carefully keeping the latter cool and adding the ammoniacal fluid very slowly and stirring all the time.

5b. *Sodium Hypochlorite* is made as follows :

Take

Chlorinated Lime 10 Gm.

Water 100 Cc.

Sodium Carbonate Solution 1 in 5..... sufficient

Put the Chloride into a mortar and mix it by rubbing with the water. Transfer the mixture to a bottle, allow to stand and draw off with a syphon the solution from the insoluble matter. To this solution add the Sodium Carbonate solution slowly and with shaking, until on filtering a small portion of the mixture no precipitate is obtained on adding a drop more Sodium Carbonate solution. Now allow the fluid to settle and draw off the clear solution for use.

5c. *Nessler's Solution* is made as follows:

Take

Potassium Iodide	3.5 Gm.
Mercuric Chloride	1.6 "
Water	30 Cc.
Potassium Hydroxide (1 in 5)	sufficient

Dissolve the Iodide in 10 c. c. of the water and the chloride in the balance, heating. Add the chloride solution to the iodide solution until a small precipitate is produced which does not disappear on stirring. Now add the Potassium Hydroxide solution until the mixture measures 100 c. c.

Allow to stand and pour off the clear fluid. To this clear fluid add more mercuric chloride solution until a small precipitate is obtained after stirring; allow to settle, and this clear fluid is ready for use.

CHAPTER I.

SEPARATION OF THE METALS INTO GROUPS.

6. For the beginner it is only necessary to consider the more common of the metallic elements and the method of separating them from one another. For this purpose the following metals are assumed to be in a single solution.

<i>Insoluble Chlorides</i>	Pb. Lead (Plumbum)	<i>Ppt. by HCl</i>
	Hg ₂ Mercurous Mercury (Hydrargyrum)	
	Ag. Silver (Argentum)	
<i>Insoluble Sulfides</i>	Hg. Mercuric Mercury	
	Bi. Bismuth	<i>Pppt. by H₂S.</i>
	Cu. Copper (Cuprum)	
	Cd. Cadmium	
	As. Arsenic	
	Sb. Antimony (Stibium)	
	Sn. Tin (Stannum)	
<i>Sulfides</i>	Co. Cobalt	<i>Pppt. by (NH₄)₂S in presence of NH₄OH</i>
	Ni. Nickel	
	Fe. Iron (Ferrum)	
	Mn. Manganese	
<i>Hydroxides</i>	Cr. Chromium	<i>Pppt. by NH₄OH.</i>
	Al. Aluminium	
	Zn. Zinc	<i>Pppt. by (NH₄)₂CO₃ in presence of NH₄OH</i>
<i>Insoluble Carbonates</i>	Ba. Barium	
	Sr. Strontium	
	Ca. Calcium	
	Mg. Magnesium	
	K. Potassium (Kalium)	
	Na. Sodium (Natrium)	
	NH ₄ . Ammonium (hypothetical)	

7. If to a solution in a test-tube containing all the above metals together we add hydrochloric acid, we shall find that only the first three (or any one) will be precipitated. In other words only these metals are capable of forming insoluble compounds with chlorine, the latter element leaving the hydrogen of the acid because it has

a stronger affinity for the metals thrown out of solution. All the chlorides of these metals have a white color.

8. Before proceeding we must find out if the amount of hydrochloric acid added has been sufficient to throw down all the Lead, Mercurous Mercury and Silver that may be in the solution. For this purpose the precipitated chlorides are allowed to settle, and a few drops more acid are added to the clear fluid above them. If this fails to produce any further precipitate the acid has done all that it will. If, on the other hand, it still causes a precipitate we must add more hydrochloric acid until the latter fails to give any more chlorides of the metals above mentioned.

9. This latter proceeding is termed "adding an excess" of the acid, and it is an extremely important step to learn in chemical analysis. If an insufficient amount of acid is added some of the metals will still remain in the solution, on the other hand if too much acid is used we are adding material to the mixture that will interfere with our future work for the separation of the other metals.

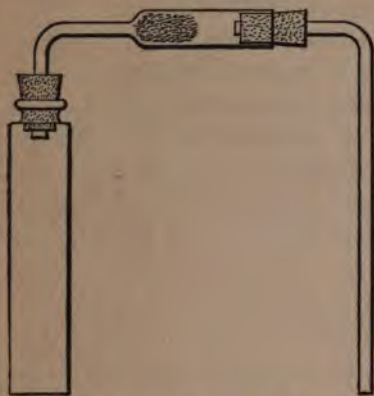
Having thus thrown down all the above mentioned metals in the manner described we pour off the fluid through a filter leaving the insoluble matter behind, and proceed with the filtrate as directed in the succeeding paragraphs. See also special tests for Bismuth and Antimony with hydrochloric acid.

The metals obtained above as chlorides may be called "the first group." The separation of the several metals from one another will be described later.

10. The filtrate from the first group of metals is now saturated with hydrogen sulphide gas. In order to do this the gas is allowed to bubble through this filtrate until it will take up no more of the same.

The apparatus shown in the annexed cut is found convenient for the generation of small quantities of Hydrogen Sulphide as used in analysis. It consists of a long eight drachm vial with a small cork carrying a tube containing a little cotton. Into the larger end of this latter tube another cork is fitted to carry the finer tube delivering the gas. To use the apparatus place in the vial some coarsely broken iron sulphide and about one inch in depth of water; now add about fifteen drops of sulphuric acid,

and give the gas a little time to start. In a few minutes a brisk effervescence takes place and the tube delivering the gas is put into the test-tube containing the solution to be saturated. If the



gas does not come off fast enough, after waiting a few minutes add to the phial five or six drops more sulphuric acid, but do not add the acid in too large quantities as the gas may come off so fast as to be unmanageable, and the fluid in the phial may flow over into the solution being saturated. The apparatus is sufficiently simple to be readily constructed by the student, as instead of the enlarged tube

carrying the cotton a tube having a cork in each end may be used for the purpose.

A good way to ascertain when the filtrate is saturated is to remove the tube delivering the gas and shake the test tube with the opening tightly closed with the thumb. If there is a pressure on the thumb when the test tube is shaken the filtrate is saturated with gas; if, on the other hand, there is a suction on the thumb, the gas must be passed through the solution again.

11. The sulphur of the hydrogen sulphide unites with the metals Mercuric Mercury, Bismuth, Copper, Cadmium, Arsenic, Antimony, and Tin, to form insoluble sulphides with them. These compounds are only completely precipitated when the filtrate from the first group is perfectly saturated with hydrogen sulphide gas. These sulphides are from the "second group" of metals. In color the sulphides of Mercury, Bismuth and Copper are black, Tin is brown or yellow, Arsenic and Cadmium are yellow, Antimony is orange. The precipitated sulphides of the metals of the second group are filtered out of the solution and the filter is set on one side for future use.

12. To the filtrate last obtained now add some ammonium chloride solution equal to about $\frac{1}{4}$ of the volume of the fluid in the test tube. To the same fluid add enough ammonium hydroxide to give it an odor of the latter after shaking. Finally add to the same mixture some ammonium sulphide.

Hydrides
Ni,
Iron,
drophides
Al.

13. The addition of the ammonium hydroxide may produce a precipitate but this is disregarded for the time being. The ammonium sulphide gives up its sulphur to the metals Cobalt, Nickel, Iron, Manganese and Zinc, while Aluminium and Chromium are precipitated as hydroxides. In color, the sulphides of nickel, cobalt and iron are black, manganese dirty pink, zinc white, chromium hydroxide pale green, and aluminium hydroxide white.

In order to ascertain if enough sulphide has been added, the solution must be filtered, and a few drops more of the ammonium sulphide mixed with the clear filtrate. Here, again, care must be taken that "an excess" of the precipitant is used, before going on to the next step in the analysis.

The mixture of sulphides and hydroxides obtained in the last case is from the "third group" of metals.

14. The filtrate from the group last obtained is mixed with ammonium carbonate solution, and thoroughly shaken. Here also the same precaution must be taken to insure "an excess" of the carbonate, as was followed in the case of ammonium sulphide.

15. The precipitate obtained may contain the metals Barium, Strontium and Calcium as carbonates. These metals unite with the carbonic acid of the ammonium carbonate to form insoluble compounds in the presence of the ammonium hydroxide. All these carbonates are white.

The precipitate so obtained is from the "fourth group" of metals.

16. In the filtrate from the ammonium carbonate precipitate we may have the metals Magnesium, Potassium and Sodium; together with Ammonium and all the chemicals added to precipitate the other groups mentioned above.

The last filtrate obtained gives us what is termed the "fifth group" of metals.

17. Since we have added ammonium salts to effect the separation of the first four groups of metals we cannot test for ammonium in the filtrate last obtained. We make a special test for ammonium in the original solution used at the beginning, and before we have added anything to it.

The various operations described above may be tabulated in the following form :

GROUP TABLE.

To the clear solution add HCl in slight excess. Filter and wash.

Ppt.*—Treat as per Table I. Contains Pb, Hg, and Ag as Chlorides.	Filtrate.—Dilute, warm and pass H ₂ S gas until thoroughly saturated. Filter and wash.
Ppt.—Treat as per Table II. Contains Pb, Hg, Bi, Cu, Cd, As, Sb and Sn as Sulphides.	Filtrate.—Add NH ₄ Cl (½ vol) then NH ₄ OH in excess, and then (NH ₄) ₂ S in slight excess. Shake well. Filter and wash.
Ppt.—Treat as per Table III. Contains Co, Ni, Fe, Mn, and Zn as Sulphides, with Cr and Al as Hydroxides.	Filtrate.—Add (NH ₄) ₂ CO ₃ in slight excess. Filter and wash.
Ppt.—Treat as per Table IV. Contains Ba, Sr and Ca as Carbonates.	Filtrate.—Treat as per Table V. Contains Mg, K, Na, and NH ₄ salts, together with all reagents added.

*Abbreviation for Precipitate.

CHAPTER II.

SEPARATION OF THE METALS OF THE FIRST GROUP.

18. In every case the group precipitate should always be washed with water to free it from the fluid that adheres to it and which contains some of the metals of other groups.

In the case of the first group, then, the first step is to wash with cold water. For this purpose use the jet of the wash bottle, throwing the stream around the edges of the filter paper in a uniform manner. Always let the first lot of water run through the funnel before adding a second quantity. Half a funnel full of water used twice will be sufficient.

Do not add the wash water to the filtrate but allow it to run into another vessel. It may be thrown away unless it is needed to dilute the filtrate to a convenient volume.

19. Transfer the group precipitate to a test tube and boil it with water, being careful not to heat the tube directly on the bottom, to avoid fracture.

After the first boiling, allow the precipitate to settle and pour off the hot fluid into another tube, setting it aside for future use. Add more water to the precipitate and boil again. This second fluid may be thrown away, it serves to dissolve out any of the chloride possibly left by the first lot of water.

20. The first hot water solution is now to be tested for lead. For this purpose the fluid is cooled and a few drops of sulphuric acid, together with a few drops of alcohol, are added to a few drops of the solution. A white precipitate of lead sulphate indicates the presence of lead, of the first group of metals.

21. The reasons for the steps taken are: Lead chloride is soluble in hot water, and lead sulphate is insoluble in a mixture of alcohol and water.

22. We now return to the precipitate insoluble in hot water. To this we add ammonium hydroxide in quantity sufficient to fill

the test tube about one-quarter full. The mixture should be thoroughly shaken and then filtered.

23. If the precipitate on the filter paper is black, mercury(ous) of the first group of metals is present.

24. To the filtrate from the black precipitate add nitric acid until the fluid turns blue litmus paper red. Shake the fluid well before testing with litmus paper. If the acid fluid gives a white precipitate it indicates the presence of silver of the first group of metals.

25. The reasons for the last steps taken are : The chloride of mercury(ous), of the first group is decomposed by ammonium hydroxide and a compound called amido-mercurous chloride is formed which has a black color and is insoluble in ammonium hydroxide. This result is very characteristic. Silver chloride, if it is in the precipitate of the metals of the first group will dissolve in the ammonium hydroxide, and by adding nitric acid to the filtrate, ammonium nitrate is formed and the silver chloride is re-precipitated.

Tabulating the operations given above the following scheme results :

TABLE I. HCl Group.

Boil the Ppt. with water, allow to settle, pour off liquid into another tube, and repeat the boiling with water. Reserve insoluble and filter the fluids hot.

Filtrate.—To part of fluid add a few drops of H_2SO_4 and alcohol. A white ppt. is $PbSO_4$ and indicates Pb.	Insoluble. Add NH_4OH , shake well and filter.
	Filtrate.—Add HNO_3 in slight excess. A white milky ppt. is $AgCl$ and indicates Ag.
	Insoluble.—Is black, and is $NH_4Hg_2Cl_2$. Indicates Hg.

CHAPTER III.

SPECIAL TESTS FOR THE METALS OF THE FIRST GROUP.

LEAD.

Blowpipe Test.

26. Heated with sodium carbonate on charcoal, lead compounds give malleable metallic globules.

Solution Tests.

27. Hydrochloric acid and soluble chlorides give a white precipitate of lead chloride PbCl_2 . Precipitate is soluble in a large quantity (1 in 135) of cold water, and more readily (1 in 30) in hot water. Hydrochloric acid and nitric acid decrease its solubility in water. In dilute solutions lead chloride will not be produced with hydrochloric acid. It is insoluble in strong alcohol; soluble in alkali acetates and thiosulphates.

28. Potassium iodide and soluble iodides give a precipitate of yellow lead iodide PbI_2 . It is soluble in 1235 parts of cold and 194 of hot water.

29. Hydrogen sulphide and soluble sulphides give a black precipitate of lead sulphide PbS . If much hydrochloric acid is present the color may be red and precipitate consists of lead chloride and lead sulphide. Lead sulphide is insoluble in cold dilute acids, alkaline hydroxides and sulphides, and potassium cyanide. Hot strong nitric acid decomposes it, forming nitrate or sulphate, or both, according to strength of acid used.

30. Alkaline hydroxides (K , Na , NH_4) give white precipitates of basic salts. With potassium and sodium hydroxides the precipitate is soluble in excess; with ammonium hydroxide it is insoluble. Soluble in dilute nitric acid. Lead acetate with ammonium hydroxide does not give a precipitate at once; a soluble acetate is formed; but a precipitate finally forms.

31. Sodium carbonate and soluble carbonates give white pre-

precipitates (often basic) more or less soluble in excess. Insoluble in potassium cyanide. Soluble in 50,500 parts of water; ammonium salts, also carbon dioxide increase the solubility.

32. Potassium chromate and soluble chromates and dichromates give a yellow precipitate of lead chromate, PbCrO_4 , soluble in potassium hydroxide and hydrochloric acid. Insoluble in acetic acid and dilute nitric acid.

33. Sulphuric acid and soluble sulphates give a fine white precipitate of lead sulphate, PbSO_4 , insoluble in water and dilute acids. Dilute solutions give precipitates only after some time, alcohol facilitates precipitation. Lead sulphate dissolves slightly in strong nitric and hydrochloric acids, is more soluble in potassium hydroxide. Ammonium acetate and ammonium salts dissolve lead sulphate; excess of sulphuric acid causes reprecipitation.

34. Commercial Lead Compounds :

Alloys :

Shot—(Lead with 40 lbs. of arsenic to the ton.)

Solder—Lead and Tin.

Type metal—Lead and Antimony.

Oxides and Salts :

Litharge—Lead Oxide, PbO .

Red Lead—Minium, Pb_3O_4 (2PbO , PbO_2).

Chrome Yellow—Lead Chromate, PbCrO_4 .

White Lead—Basic Lead Carbonate 2PbCO_3 , Pb(OH)_2 .

Sugar of Lead, Lead Acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ Soluble 1 in 1.5 of water.

Goulard's Solution—Basic Lead Acetate, $\text{PbO}(\text{C}_2\text{H}_3\text{O}_2)_2$. (Solution-25%)

Puce Lead Oxide—Lead Dioxide, PbO_2 .

Lead Iodide PbI_2 .

“ Nitrate, $\text{Pb}(\text{NO}_3)_2$, Soluble 1 in 2 of water.

MERCURY.

Blowpipe Tests.

35. All mercury compounds are volatile when heated.

Heated in a closed tube with dry sodium carbonate, metallic mercury is obtained in fine globules.

Solution Tests.

Mercurous Compounds.

36. Hydrochloric acid and soluble chlorides give a white precipitate of mercurous chloride, Hg_2Cl_2 , insoluble in hydrochloric acid and nitric acid. Aqua Regia and chlorine water dissolve it, forming mercuric chloride. Potassium and sodium hydroxides decompose it, giving mercurous oxide. Ammonium hydroxide gives amido-mercurous chloride, $\text{NH}_2\text{Hg}_2\text{Cl}$. All these latter are black.

37. Potassium iodide and soluble iodides give precipitates of green mercurous iodide, Hg_2I_2 , which is slightly soluble in water.

38. Hydrogen sulphide and soluble sulphides, give a black precipitate of mercuric sulphide, and mercury, HgS, Hg . It is insoluble in dilute acids, ammonium sulphide, and potassium cyanide. Sodium sulphide and hydro-sulphide dissolve the precipitate; in the first case mercury separates. It is readily soluble in Aqua Regia.

39. Alkaline hydroxides ($\text{K}, \text{Na}, \text{NH}_4$) give a precipitate of black mercurous oxide with the first two (K, Na), and an amido-mercurous compound with the last (NH_4). All are insoluble in excess.

Mercuric Compounds.

40. Hydrogen sulphide and soluble sulphides, give a black precipitate of mercuric sulphide, HgS . If the reagent is added in small quantities the precipitate is first white, then yellow, orange and red, finally black.

These colors are due to double compounds of the salt in solution and mercuric sulphide. Mercuric sulphide is almost insoluble in ammonium sulphide, especially if the latter is yellow. It is insoluble in potassium hydroxide, and cyanide, and also in nitric acid, even on boiling the last. Hot hydrochloric acid dissolves it. Potassium and sodium sulphides mixed with the hydroxides dissolve it; but the hydrosulphides do not. Aqua Regia decomposes and dissolves it.

41. Potassium iodide and soluble iodides give a scarlet precipitate of mercuric iodide, HgI_2 . It is soluble in excess of the precipitant used and also in mercuric chloride.

42. Potassium and Sodium hydroxides give precipitates of mercuric oxide (yellow). With small quantities of hydroxide the precipitate is red-brown and contains basic salt. Excess of the hydroxide finally gives mercuric oxide. Yellow mercuric oxide is insoluble in excess of the hydroxide.

43. Ammonium hydroxide gives a precipitate of white amido-mercuric compounds which are variable in composition. With mercuric chloride the precipitate is amido-mercuric chloride, NH_2HgCl , and is insoluble in excess of the hydroxide, but soluble in hydrochloric acid.

44. Commercial Mercury Compounds :

Alloys : (Amalgams.)

Mirror amalgam—mercury and tin.

Electric “ —mercury, zinc and tin.

Gold “ (dental)—mercury and gold.

Cadmium “ (“)—mercury and cadmium.

Oxides and Salts :

Red precipitate—mercuric oxide HgO .

Black wash—mercurous oxide Hg_2O (calomel and lime water).

Calomel—mercurous chloride Hg_2Cl_2 .

Corrosive sublimate—mercuric chloride HgCl_2 , soluble 1 in 16 of water; 1 in 3 of alcohol.

Green iodide of mercury—mercurous iodide Hg_2I_2 .

Red iodide of “ mercuric iodide HgI_2 .

Fusible white precipitate—diammonium mercuric chloride $(\text{NH}_4)_2\text{HgCl}_2$.

Infusible white precipitate—amido-mercuric chloride NH_2HgCl .

Vermilion—mercuric sulphide HgS .

SILVER.

Blowpipe Tests.

45. Under favorable heating with sodium carbonate on charcoal, white bright metallic globules are obtained.

Solution Tests.

46. Hydrochloric acid and soluble chlorides give a white curdy precipitate of silver chloride AgCl . It is insoluble in nitric

acid but soluble in ammonium hydroxide. The chloride in the ammonium hydroxide is reprecipitated by excess of nitric acid. Strong hydrochloric acid and strong solutions of alkaline chlorides dissolve silver chloride, but it is precipitated on diluting.

47. Hydrogen sulphide and soluble sulphides give a black precipitate of silver sulphide Ag_2S . It is insoluble in dilute acids, alkaline hydroxides and sulphides, but dissolves in potassium cyanide. It is soluble in boiling nitric acid.

48. Alkaline hydroxides (K, Na) give a gray-brown precipitate of silver oxide Ag_2O , insoluble in excess of the precipitants, but soluble in ammonium hydroxide.

49. Ammonium hydroxide in small quantity gives a brown precipitate of silver oxide soluble in excess of the precipitant. Acid solutions are not precipitated.

50. Commercial Silver Compounds :

Alloy :

Silver coin—silver and copper.

Oxides and Salts :

Silver oxide— Ag_2O .

Silver nitrate— AgNO_3 Soluble, 1 in 0.8 part of water; 1 in 26 parts of alcohol.

Lunar caustic—fused silver nitrate.

Silver cyanide— AgCN .

Silver Iodide— AgI . Used in pharmacy and photography.

“ Bromide— AgBr . Used in photographic dry plates.

CHAPTER IV.

SEPARATION OF THE METALS OF THE SECOND GROUP.

As in the first group, the precipitate should be washed with water, to take out of it any adhering fluid containing metals of other groups. Use the wash bottle in the same manner as there described, and water in the same quantity. The same precaution must be taken about not adding the wash water to the filtrate.

51. Place some of the precipitate, after washing, into a test tube, and pour upon it about five times its volume of ammonium sulphide, and shake well.

This treatment serves to separate the metallic sulphides in the precipitate in two parts, those soluble in ammonium sulphide being arsenic, antimony and tin sulphides. The mixture is now filtered, and the insoluble part is washed. On the filter paper will be found any or all of the sulphides of the metals: lead (only partially precipitated by hydrochloric acid in group I), mercury, bismuth, copper and cadmium.

Set the solution aside for the present, and proceed with the insoluble part as follows:

52. SULPHIDES INSOLUBLE IN AMMONIUM SULPHIDE.—Dry the washed precipitate by placing the filter paper, unfolded, over a small gas flame, and at such a distance above it that the paper is not charred. Dry till the precipitate can be readily scraped off the paper with a knife.

53. Put the dry material into a porcelain dish and add to it enough Aqua Regia (1 volume of nitric acid and 2 volumes of hydrochloric acid) to make it thoroughly wet. Do not use more acid than necessary. Heat the acid mixture very gently until all the dark matter is changed to a yellowish color, which is sulphur, and then continue the heating till only a few drops of fluid remain in the dish. Be very careful not to bake the material in the dish, moving the fluid around the sides of the dish as it evaporates, leaving the matter still moist when the work is complete.

54. Now add to the contents of the dish a few drops of sulphuric acid and only enough to make the mass perfectly fluid. Heat the dish again till heavy white fumes of sulphuric acid are given off, and then cover it with another dish and allow to cool.

55. The preceding steps are taken to turn the sulphides, first into chlorides by Aqua Regia, and then into sulphates by the sulphuric acid. If the chlorides become overheated during the evaporation of the acid, they may be turned into compounds that will not give sulphates with the sulphuric acid, hence it is important to take the precautions given above.

56. After the dish is cool (*it must be cool*) add to the fluid in it enough water to dilute the acid to ten times its volume, and stir well. Allow the insoluble matter to settle, pour the fluid off into a test tube, and add a few more drops of sulphuric acid, and, then, ten times its volume of water to the contents of the dish, and stir well again. By this treatment all the soluble matter will be dissolved out. Pour off the second lot of water into the tube that contains the first portion used, and filter the combined fluids. The insoluble material is lead sulphate, and indicates that this group contains lead not precipitated by hydrochloric acid. This lead sulphate should be a fine, very heavy, white precipitate, in the bottom of the dish; but if the dry precipitate of sulphides insoluble in ammonium sulphide, contains any filter paper removed during the scraping, see **52**, then it may be dark colored.

57. The filtered fluid from the lead sulphate now contains the other metals, mercury, bismuth, copper and cadmium, as sulphates.

58. Place a few drops of the fluid in a watch glass and put into it a clean piece of copper wire. Allow this to stand for a few minutes, and if a gray deposit forms on the wire, which when rubbed with the finger gives a bright white metallic surface, mercury is present in the group, the deposit being fine globules of mercury precipitated by the copper. Having used copper in the watch glass, we must throw this fluid away.

59. The rest of the solution **57** from which a few drops were taken is next mixed with ammonium hydroxide till it is distinctly alkaline after shaking well. Filter out the precipitate formed and wash it well with three lots of water.

Set the filtrate aside for the present and proceed with the precipitate as follows :

60. Dissolve the well washed precipitate off the filter paper with the least possible quantity of hydrochloric acid, using a few drops. Boil down the acid fluid till only enough remains in the test tube to allow one or two drops to be poured out. Pour these drops into a tube full of cold water. If a fine white cloud forms after some minutes, it is bismuth oxychloride, and indicates the presence of bismuth.

61. The precipitate formed by ammonium hydroxide may be a compound of mercury together with bismuth hydroxide. The solution in hydrochloric acid converts both these into chlorides ; the bismuth chloride gives an insoluble oxychloride with water, while the mercury chloride is left in the solution, hence the above treatment serves to distinguish them. Care must be taken that the fluid poured into the water does not contain too great an excess of acid, and this is the reason for boiling the fluid down to a few drops.

62. Now return to the filtrate from the ammonium hydroxide precipitate (see **59**). This contains the copper and cadmium. If it has a blue color, copper is present in this group. In order to find cadmium in this fluid, proceed as follows :

63. To the solution add acetic acid till the fluid is acid to test-paper. Pass through the fluid hydrogen sulphide until it is saturated, and filter out the precipitate formed. This precipitate contains both copper and cadmium as sulphides. The filtrate from these is thrown away. If the precipitate with hydrogen sulphide is yellow, cadmium is present, and the operation in **64** and **65** may be omitted, copper and mercury being absent.

64. The mixed sulphides of copper and cadmium are washed on the filter as usual, the filter is pierced with a glass rod and the precipitate is washed into a test-tube with dilute sulphuric acid (1 in 6), and the mixture is boiled for some minutes. By this treatment the cadmium sulphide dissolves while the copper sulphide remains. Filter out the copper sulphide, and it may be thrown away. The matter insoluble in sulphuric acid may also be mercuric sulphide if that metal has already been found. Copper is not

present unless it has given a blue color with ammonium hydroxide. To the solution add ammonium hydroxide till the fluid is just alkaline, then add hydrochloric acid, drop by drop, till the fluid is just acid. Cool the fluid and pass hydrogen sulphide through it until it is saturated. If a yellow precipitate forms, it is cadmium sulphide, and indicates the presence of cadmium.

65. The reasons for the last steps are: Sulphuric acid has the property of dissolving cadmium sulphide, and if it is not too strong it will not dissolve copper sulphide; it is therefore important to dilute the acid as above. The acid fluid containing the cadmium cannot readily be precipitated by hydrogen sulphide, and the acid has to be neutralized by ammonium hydroxide; then a few drops of hydrochloric acid bring it into the proper condition for the use of hydrogen sulphide. Cadmium sulphide is insoluble in weak hydrochloric acid.

66. SULPHIDES SOLUBLE IN AMMONIUM SULPHIDE.—The fluid filtered from the insoluble matter examined above may contain the sulphides of arsenic, antimony and tin.

67. These are thrown out of solution when the fluid is made acid. Add hydrochloric acid to the solution *a few drops at a time* (shaking between each addition) till it is just acid to test-paper. We now obtain a precipitate of the sulphides, mixed with *sulphur* from the decomposition of the ammonium sulphide by the acid.

68. Filter out the precipitate and wash it. The filtrate may be thrown away.

Put the precipitate into a tube and shake it with about four times its volume of ammonium carbonate. This last solution will dissolve the arsenic sulphide, and the other sulphides will remain insoluble. Filter out the insoluble matter and wash it.

69. To the ammonium carbonate filtrate add hydrochloric acid *slowly*, shaking between each addition, till the fluid is just acid to test-paper. If arsenic is present, a bright yellow precipitate will form.

70. Sometimes a brownish precipitate will form; this is due to a little copper sulphide, and its presence may be proved by filter-

ing out the precipitate, dissolving in a few drops of nitric acid and adding ammonium hydroxide in slight excess ; if a blue color is produced, copper is present. The presence of copper at this point is due to the slight solubility of copper sulphide in the ammonium sulphide used to separate the members of this group into two parts at the beginning of operations.

71. The yellow precipitate of arsenic sulphide may be washed and examined by special tests given later.

72. After washing the precipitate insoluble in ammonium carbonate, it must be dried as in the case of the sulphides insoluble in ammonium sulphide at the beginning of this group (see **52**). The dried material is put into a dish and made thoroughly wet with hydrochloric acid. Heat the acid mixture until only *yellow sulphur* is left. Apply the heat carefully and do not bake the mixture. If the acid boils away, add a few drops more, but do not use too much. As soon as the precipitate is all acted upon and only the sulphur remains, add water to the contents of the dish to about four times the volume of the acid that remains. If the water gives a milky fluid, too much water has been added ; in this case add carefully a few drops more of acid till it clears up. Filter out the sulphur and let the fluid run into another dish. Place in the bottom of the last dish a piece of platinum foil that is bright and has been made red hot in gas flame. On the platinum foil place a piece of sheet zinc that has been cleaned by washing in dilute hydrochloric acid. A brisk effervescence should now take place on the zinc, and if it does not, add a few drops more of hydrochloric acid. If a deep black deposit forms on the platinum, antimony is present in this group. The stain on the platinum foil may also be due to copper, the sulphide of which is soluble in ammonium sulphide (see **70**), but it is then a brownish stain. Allow the action to go on for some time, and watch for the presence of gray metallic particles floating about in the fluid and in the bottom of the dish. On the zinc also some of these particles may adhere.

With the finger rub the particles off the zinc into the fluid in the dish, using a little water from the wash bottle to wash the fingers. Remove the platinum from the dish ; wash it also, and allow the contents of the dish to deposit. Pour off the fluid as much as

possible ; then drain the deposit, and add a few drops of hydrochloric acid to what remains in the dish, heating gently till the matter is dissolved. When solution is complete, pour it into a test-tube, and add to the fluid a few drops of mercuric chloride. A white precipitate indicates the presence of tin in this group. The precipitate is mercurous chloride, and is due to the action of tin (stannous) chloride on mercuric chloride.

74. The reasons for the steps in the second part of this group are as follows: The addition of hydrochloric acid to the ammonium sulphide filtrate neutralizes the solvent effect of the fluid, and the sulphides are separated. As the filtrate from these reprecipitated sulphides contains only ammonium chloride, we throw it away. The treatment with ammonium carbonate is a simple solution of the arsenic sulphide, and the addition of acid neutralizes this solvent action and gives the yellow arsenic sulphide. Heating the sulphides, insoluble in ammonium carbonate, with hydrochloric acid, serves to convert them into chlorides. The milky appearance sometimes obtained on adding water to the chloride solution is due to the formation of antimony oxychloride, which is soluble in hydrochloric acid. The black stain on the platinum is metallic antimony, precipitated by the zinc ; the gray particles are metallic tin, due to the same action. Heating the tin with hydrochloric acid gives stannous chloride, and this latter takes chlorine from mercuric chloride, which is soluble, reducing it to mercurous chloride, which is insoluble.

The foregoing description is tabulated in the following scheme :

TABLE II. H,S Group.

Add dilute (NH₄)₂S, shake well, warm, filter and wash.

<p>Insoluble.—Drain and dry. Dissolve all (except S) in Aqua Regia (1 HNO₃, 2 HCl) using only a few drops. Boil off excess of acid, <i>but do not dry</i>. Add few drops of H₂SO₄, heat till white fumes appear, cool, add water, stir well and filter, repeat treatment with water.</p>		<p>Filtrate.—Add HCl in slight excess, filter, wash ppt. and reject filtrate.</p>
<p>Residue Is PbSO₄ and indi- cates Pb.</p>	<p>I.—Small in W. G. Add clean Cu wire. Metallic coat is Hg.</p>	<p>Ppt. Warm with (NH₄)₂CO₃ and filter.</p>
	<p>Filtrate—Divide in two parts. II.—Large. Add NH₄OH in excess, shake well and filter.</p>	<p>Filtrate.—Add HCl in slight excess. Yellow ppt is As₂S₃, and indicates As. Confirm by special tests.</p>
	<p>Ppt.—Wash well. Dissolve in few drops HCl. Evaporate off excess of acid. Pour into cold water. White cloud is BiOCl and indicates Bi</p>	<p>Insoluble.—Wash, dry, boil with HCl, till all dissolved except S, dilute with little water, filter into dish, add Pt and Zn. Black stain on Pt indicates Sb. Wash the black sediment, drain off the water, dry, add HCl and warm till dissolved. Dilute with little water, put into test tube and add HgCl₂. A white ppt. is Hg₂Cl₂ and indicates Sn.</p>

CHAPTER V.

SPECIAL TESTS FOR THE METALS OF THE SECOND GROUP.

The special tests for mercury and lead are given on pages 21 and 22.

BISMUTH.

Blowpipe Test.

75. Heated on charcoal with sodium carbonate in the reducing flame, bismuth compounds give brittle metallic globules. Heated with a mixture of sulphur and potassium iodide, they give a scarlet coat to the charcoal which is highly characteristic.

Solution Tests.

76. Hydrochloric acid and soluble chlorides give a white precipitate of bismuth oxychloride, BiOCl , if there is not too much free acid present. The precipitate is insoluble in water, but it dissolves in strong acids. If a solution gives a precipitate with hydrochloric acid, and if this disappears on adding a few drops of the fluid containing the precipitate to a few drops of hydrochloric acid, the solution cannot contain any of the members of the first group of metals. Small quantities of lead may be dissolved; but these are found in the second group. The precipitate soluble in hydrochloric acid may be either bismuth or antimony. See Special Tests for Antimony.

77. Hydrogen sulphide and soluble sulphides give a brownish-black precipitate of bismuth sulphide Bi_2S_3 in acid or neutral solutions. Presence of much acid prevents the precipitation. The precipitate is insoluble in dilute acids, alkalies, alkaline sulphides and potassium cyanide. It is soluble in strong nitric acid.

78. Alkaline hydroxides ($\text{K}, \text{Na}, \text{NH}_4$) give white precipitates of bismuth hydroxide, insoluble in excess of the precipitant.

79. Sodium carbonate and soluble carbonates give a white precipitate of basic bismuth carbonate BiO_2CO_3 , insoluble in excess of the precipitant and in potassium cyanide.

80. Potassic chromate and soluble chromates and dichromates give a yellow precipitate of basic bismuth chromate, of various composition. The precipitate is soluble in dilute nitric acid, and insoluble in potassium hydroxide. Compare lead chromate (see 82).

81. Sulphuric acid and soluble sulphates do not give precipitates with bismuth compounds.

82. Water precipitates basic salts. Thus, solution of bismuth nitrate, diluted with water, gives bismuth basic nitrate, BiONO_3 ; and solution of bismuth chloride, under like circumstances, gives bismuth basic chloride, BiOCl .

83. Commercial Bismuth Compounds:

Alloys:

Wood's alloy for dentists. Bi 4, Pb 2, Sn 1, Cd 1.

Type metal sometimes contains 2 per cent. of Bi.

Oxides and Salts:

Bismuth cream, BiO_3H_3 , 20 parts in 100 of water.

Bismuth subcarbonate, $\text{Bi}_2\text{O}_3\text{CO}_3\text{H}_2\text{O}$. } Formulæ are uncertain.

Bismuth subnitrate, $\text{BiONO}_3\text{H}_2\text{O}$. }

Bismuth citrate, $\text{BiC}_6\text{H}_5\text{O}_7$.

Flake white is bismuth subnitrate.

Pearl white is bismuth subchloride.

Blowpipe Tests.

84. Heated in the reducing flame, copper compounds give red metallic globules. These are very small and may not be perceptible without a lens.

85. On platinum wire. In the flame, when copper compounds are moistened with hydrochloric acid, a sky-blue color is produced, fading to emerald green.

86. Borax in a bead gives a green glass while hot and blue when cold.

Solution Tests.

87. Hydrochloric acid and soluble chlorides give a green color to copper solutions.

88. Hydrogen sulphide and soluble sulphides give a brown-black precipitate of copper sulphide, CuS . This is formed in neutral, acid, and alkaline solutions. It is insoluble in dilute acids and alkaline hydroxides. Sulphides of sodium and potassium do not dissolve it. Ammonium sulphide dissolves it slightly. Nitric acid dissolves it on boiling. Dilute sulphuric acid does not dissolve it on boiling. Potassium cyanide dissolves the freshly formed precipitate. Much acid in solutions will prevent the formation of the precipitate of copper sulphide.

89. Alkaline hydroxides (K and Na) give a light blue precipitate of copper hydroxide $\text{Cu}(\text{OH})_2$. Boiling displaces water and gives black copper oxide. The blue hydroxide dissolves in a large excess of either potassium or sodium hydroxide, giving a blue fluid. Organic acids prevent the formation of copper hydroxide.

90. Ammonium hydroxide in small quantity gives the same light blue precipitate as sodium hydroxide. With more ammonium hydroxide, a blue solution is formed.

91. Sodium carbonate and soluble carbonates (except of NH_4) give a greenish-blue precipitate of basic copper carbonate CuO_4HCO_3 . It is soluble in ammonium hydroxide to a blue fluid, and in potassium cyanide without any color. Boiling the precipitate turns it brown.

92. Ammonium carbonate acts like ammonium hydroxide.

93. Potassium ferrocyanide gives a reddish-brown precipitate of copper ferrocyanide $\text{Cu}_2\text{Fe}(\text{CN})_6$, insoluble in dilute acids and decomposed by alkaline hydroxides. In very dilute solutions only a red color is produced.

94. Commercial Copper Compounds :

Alloys :

Brass—copper and zinc.

Bronze—copper, tin and zinc.

Bell Metal—copper and tin.

Speculum Metal—copper and tin.

German Silver—copper, zinc, nickel.

Aluminium Bronze—copper with 10% Al.

Oxides and Salts :

Black Oxide,— CuO , Cupric Oxide.

Red Oxide— Cu_2O , Copper Scale. Suboxide. Cuprous Oxide.

Blue Vitriol,— $\text{CuSO}_4 + 5\text{H}_2\text{O}$, Cupric Sulphate. Blue-stone.
Soluble 1 in 2.6 of water.

Scheele's Green—Cupric Arsenite, CuHAsO_3 .

Paris Green.—Aceto-arsenite of copper. Composition variable.

Verdigris—Basic Cupric Acetate. Composition variable.

Copper Acetate— $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$. Soluble 1 in 15 of water ; 1 in 135 of alcohol.

CADMIUM.

Blowpipe Tests.

95. Not very characteristic for this metal.

Solution Tests.

96. Hydrochloric acid and soluble chlorides do not affect cadmium solutions.

97. Hydrogen sulphide and soluble sulphides give a bright yellow precipitate of cadmium sulphide CdS in alkaline, acid and neutral solutions. It is insoluble in dilute acids, alkaline hydroxides and sulphides and potassium cyanide. It is soluble in boiling nitric acid, also in boiling hydrochloric acid and boiling dilute sulphuric acid (compare copper sulphide). Much acid in solutions will prevent precipitation of cadmium sulphide.

98. Alkaline hydroxides (K and Na) give a white precipitate of cadmium hydroxide, $\text{Cd}(\text{OH})_2$, insoluble in excess of the precipitant.

99. Ammonium hydroxide in small quantity gives a white precipitate of cadmium hydroxide which is soluble in excess ; but it is precipitated on diluting and by potassium or sodium hydroxides.

100. Alkaline carbonates (K, Na and NH_4) give a white precipitate of cadmium carbonate, CdCO_3 , insoluble in excess, except ammonium carbonate which dissolves a little. Ammonium salts retard the precipitation, ammonium hydroxide prevents it. The precipitate is soluble in potassium cyanide.

101. Commercial Cadmium Compounds :

Alloys:

Fusible alloys—bismuth, lead, tin and cadmium.

Wood's alloy—see Bismuth alloys.

Oxides and salts:

Cadmium yellow— CdS cadmium sulphide. An artist's pigment.

Cadmia—same as preceding. Some varieties contain thallium.

ARSENIC.**Blowpipe Tests.**

102. Arsenic compounds heated on charcoal with sodium carbonate give an odor of garlic. This is very characteristic.

103. Heated in a closed glass tube with potassium cyanide and sodium carbonate (1 KCN with $3 \text{ Na}_2\text{CO}_3$), arsenic compounds give a black mirror of arsenic. On opening the closed end of the tube and heating the mirror in a current of air, white octohedra of arsenious oxide are deposited in the upper part of the tube.

104. Arsenious and arsenic oxides heated in a glass tube, in the upper part of which is some red hot charcoal, are decomposed and a black mirror of arsenic is formed above the charcoal.

Solution Tests.*Arsenious Compounds.*

105. Hydrochloric acid and soluble chlorides do not affect arsenious solutions.

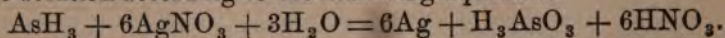
106. Hydrogen sulphide and soluble sulphides in acid solutions give a yellow precipitate of arsenious sulphide, As_2S_3 . It is soluble in alkaline sulphides, hydroxides, carbonates and acid-carbonates. These solutions are reprecipitated by the addition of hydrochloric acid in excess, alone, or with more hydrogen sulphide. The precipitate is soluble in boiling nitric acid. It is nearly insoluble in boiling hydrochloric acid. On fusing the dry precipitate with sodium carbonate and nitrate, sodium arsenate and sulphate are formed. A water solution of arsenious acid is not precipitated by hydrogen sulphide; a yellow color only is given until hydrochloric acid is added, when yellow arsenious sulphide falls. The addition of acid is also necessary in the case of alkaline arsenites.

107. Silver nitrate in neutral solutions gives a yellow precipitate of silver arsenite Ag_3AsO_3 . It is soluble in nitric acid and in ammonium hydroxide. It is also soluble in ammonium nitrate to a slight extent. From the last fact a small quantity of arsenious sulphide dissolved in much nitric acid and neutralized with ammonium hydroxide would not give the silver arsenite.

108. Copper sulphate in neutral solutions gives a yellowish-green precipitate of copper arsenite, CuHAsO_3 (Scheele's Green). It is soluble in alkaline hydroxides.

109. Copper foil, clean and bright, heated with a solution containing hydrochloric acid, becomes coated with a film of iron-gray copper arsenide, Cu_3As_2 (Reinsch's test). By drying the carefully washed coated copper and heating in a glass tube, a mirror of arsenic may be obtained.

110. Zinc and sulphuric acid added to a solution containing arsenic give hydrogen arsenide, AsH_3 . The best method to pursue with this (Marsh's test) is to make an apparatus for generating hydrogen gas, with a drying tube attached filled with granulated calcium chloride, and a length of hard glass tubing terminating in a jet. The hard tube should be horizontal and the jet vertical. At various points on the horizontal tube the glass should be drawn out to make the tube smaller. When the apparatus is ready, place in it some zinc (free from arsenic) and cover it with water. Now pour in a little sulphuric acid (also free from arsenic) and shake the apparatus. Continue adding acid and shaking till a good supply of hydrogen gas is given off and all air is expelled from the apparatus. Now add the arsenic solution to be tested and heat the horizontal tube near the contracted parts, and on the side toward the hydrogen apparatus. The arsenic will form a black mirror on the tube just beyond the heated part. If the gas is ignited at the jet, and a piece of cold porcelain is held down in the flame, it will be coated with a mirror of arsenic. This mirror is soluble in a solution of calcium hypochlorite (bleaching powder); compare antimony **127**. On passing the gas through a solution of silver nitrate, a precipitate of silver is produced, and arsenious acid goes into solution according to the following equation:



Compare with antimony.

111. N. B.—Great care must be taken to insure the absence of arsenic in the zinc and sulphuric acid used in the Marsh test. It is best to test the gas by heating one part of the tube for some time before adding the arsenic solution. *It is also essential that the air in the apparatus be fully displaced by hydrogen before lighting the gas or heating the tube. Cover the apparatus with a towel before lighting the jet.*

Arsenic Compounds.

112. Hydrochloric acid and soluble chlorides do not affect arsenic solutions.

113. Hydrogen sulphide and soluble sulphides do not precipitate neutral or alkaline solutions. In acid solutions the arsenic compounds are partially reduced by the sulphide to arsenious compounds, sulphur separating, and then arsenious sulphide, As_2S_3 , together with arsenic sulphide, As_2S_5 , is precipitated. This change takes some time, and may be assisted by heat at 70°C . If the solution is first mixed with sulphurous acid (or sodium sulphite and hydrochloric acid) and heated, the arsenic compounds are reduced and hydrogen sulphide gives a precipitate of arsenious sulphide.

114. Silver nitrate, in neutral solutions, gives a reddish-brown precipitate of silver arsenate, Ag_3AsO_4 , soluble in nitric acid and ammonium hydroxide. It is also soluble in ammonium nitrate to a slight extent; therefore a nitric acid solution of small quantities of arsenic acid may not give a precipitate when neutralized with ammonium hydroxide.

115. Copper sulphate, in neutral solutions, gives a greenish-blue precipitate of copper arsenate, CuHAsO_4 .

116. Magnesium mixture (magnesium sulphate, ammonium chloride and ammonium hydroxide) gives a crystalline precipitate of ammonio-magnesium arsenate, $\text{MgNH}_4\text{AsO}_4$. This precipitate may be tested for arsenic acid by dissolving a little of it in a few drops of nitric acid, adding silver nitrate, and carefully neutralizing with ammonium hydroxide; a reddish-brown precipitate of silver arsenate will be formed. This marks the difference from the phosphate compound (see magnesium **323**).

117. Copper foil acts the same as with arsenious compounds, but the solution must be mixed with twice its volume of strong hydrochloric acid.

118. Zinc and sulphuric acid act as with arsenious compounds.

119. Molybdic acid in nitric acid gives no precipitate in the cold, but on heating, a bright yellow precipitate is formed, even in dilute solutions. The precipitate is soluble in ammonium hydroxide, and this solution gives the precipitate with magnesium mixture.

120. Commercial Arsenic Compounds :

Alloys :

Shot—Lead with 2% As.

Oxides and salts :

Arsenic—White arsenic— As_2O_3 , arsenious oxide.

Realgar— As_2S_3 , red orpiment.

Orpiment— As_2S_3 , yellow orpiment—King's yellow (mixture: As_2S_3 and As_2O_3).

Scheele's green—Copper arsenite, CuHAsO_3 —Emerald green.

Paris green—Aceto-arsenite of copper, composition variable.

Sodium arsenate, Na_2HAsO_4 —soluble 1 in 4 of water.

Fowler's solution—1% of arsenious oxide in potassium carbonate solution.

ANTIMONY.

Blowpipe Tests.

121. Antimony compounds heated with sodium carbonate on charcoal in the reducing flame, give brittle metallic globules.

Solution Tests.

122. Hydrochloric acid and soluble chlorides behave with antimony compounds the same as with bismuth compounds (see **76**).

123. Hydrogen sulphide and soluble sulphides in acid solutions give a precipitate of reddish-orange antimonious sulphide Sb_2S_3 . It is soluble in alkaline (K and Na) hydroxides and sulphides; slightly soluble in ammonium hydroxide; and nearly insoluble in ammonium carbonate. It is soluble in strong hydrochloric acid, and insoluble in the dilute acid. If the dry precipitate is fused with sodium carbonate and nitrate, sodium antimonate is formed and sodium sulphate.

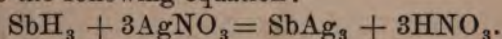
124. Alkaline hydroxides (K, Na and NH_4) give a white precipitate of antimonious hydroxide. It is nearly insoluble in ammonium hydroxide, and dissolves in the others (K and Na hydroxides).

125. Alkaline carbonates (K, Na and NH_4) give the same precipitate as the hydroxides. It dissolves in boiling sodium carbonate.

N. B.—Tartar-emetic is not perfectly precipitated by either alkaline hydroxides or carbonates.

126. Zinc added to a solution gives a black precipitate of antimony. Nitric acid must be absent. If this test is made in the presence of platinum foil, the zinc being in contact with the foil, a black or brown stain will be produced. This test is delicate and characteristic. The stain is insoluble in hydrochloric acid, but is soluble in hot nitric acid.

127. Zinc and sulphuric acid added to a solution containing antimony give hydrogen antimonide SbH_3 . As in the case of arsenic, the best method to pursue in this test (Marsh's) is to make an apparatus for generating hydrogen gas, and to follow very carefully the directions given under arsenic for the same test, **110**. On heating the tube near the contracted parts, a black mirror will deposit in the same manner as with arsenic. By holding a piece of cold porcelain in the ignited jet of gas, a deposit similar to that obtained with arsenic will also be obtained; but in the case of the antimony mirror, the deposit is not soluble in solution of calcium hydrochlorite (bleaching powder) compare arsenic, **110**. On passing the gas into a solution of silver nitrate, a black precipitate of silver antimonide, Ag_3Sb , will be obtained. This is formed according to the following equation:



128. Water precipitates basic salts from acid antimony solutions. In the case of antimony chloride, the precipitate is SbOCl , and is soluble in tartaric acid. Compare Bismuth. Presence of much free acid prevents the precipitation.

129. Commercial Antimony Compounds:

Alloys:

Type metal—Antimony and Lead.

Regulus—Commercial metallic antimony.

Britannia—Tin 80, Antimony 10, with a little copper.

Oxides and salts :

Flowers of antimony— Sb_2O_3 .

Antimony ash— Sb_2O_4 from roasted sulphide.

Potassium metantimonate— $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 + 6\text{H}_2\text{O}$, soluble in water.

Sodium metantimonate— $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 + 6\text{H}_2\text{O}$, insoluble in water.

Butter of antimony— SbCl_3 .

Powder of algaroth— SbOCl .

Antimony sulphide— Sb_2S_3 .

Kermes mineral— Sb_2O_3 and Sb_2S_3 .

Liver of antimony— K_3SbS_3 .

Tartar-emetic— $2\text{KSbOC}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$.

TIN.

Blowpipe Tests.

130. Heated with sodium carbonate and potassium cyanide on charcoal globules of metal are obtained.

Solution Tests.

131. Hydrochloric acid and soluble chlorides do not affect tin solutions.

(**132.** Hydrogen sulphide gives a brown precipitate of SnS with stannous compounds, and a yellow one of SnS_2 with stannic compounds in acid solutions. Both precipitates are soluble in yellow ammonium sulphide, and on adding acid to this solution yellow stannic sulphide is precipitated, even if stannous sulphide was the one dissolved. Both sulphides are insoluble in ammonium carbonate. Boiling hydrochloric acid dissolves both sulphides.

133. Zinc in presence of hydrochloric acid gives a precipitate of metallic tin as heavy gray particles. These are soluble in boiling strong hydrochloric acid.

(**134.** Mercuric chloride gives with stannous salts a white precipitate of mercurous chloride (see **36**). •Stannic salts do not give this test.

135. Nitric acid heated with both stannous and stannic compounds gives insoluble metastannic acid. Hence nitric acid and

nitrates should not be present in the solutions used in making tests.

136. Commercial Tin Compounds :

Alloys :

Britannia—Tin, 80 ; antimony 10, with a little copper.

Pewter—Tin and lead, 4 to 1.

Solder—Tin and lead, variable.

Bronze, gun metal, bell metal, speculum metal—Tin and copper in various proportions.

Block Tin—Commercial metallic tin.

Tin or tin plate—Sheet iron coated with tin.

Oxides and Salts :

Putty Powder— SnO_2 with PbO .

Sodium Stannate, dyers' mordant— Na_2SnO_3 .

Tin crystals, tin salts— $\text{SnCl}_2 + 2\text{H}_2\text{O}$.

Nitromuriate of tin— SnCl_4 —Pink salt— $2\text{NH}_4\text{Cl} + \text{SnCl}_4$.

Mosaic gold bronze powder— SnS_2 .

*Lft. Co, Ni, Fe, Mn & Zn as sulphides
Al & Cr as hydroxides.*

CHAPTER VI.

SEPARATION OF THE METALS OF THE THIRD GROUP.

The washing of the precipitate must be done well.

137. Warm the precipitate with about four times its volume of diluted hydrochloric acid (one volume of the strong acid and two of water), then heat the mixture till it is just warm to the hand. Filter out the matter not dissolved and wash it. This contains the cobalt and nickel sulphides which are insoluble in dilute hydrochloric acid, while the iron, manganese, and zinc sulphides, together with the aluminium and chromium hydroxides go into solution as chlorides. Put the solution aside for the time being (See 140); if it is pink, a little cobalt sulphide has dissolved.

138. Test the insoluble matter in a bead of borax. For this purpose make a loop on the end of a piece of platinum wire by winding it round the point of a lead pencil, heat the wire loop to redness and, while it is still hot, put it into some powdered borax. By this procedure the borax will adhere to the wire, and on heating it, a bead of clear borax glass will form in the loop. Care must be taken that the loop on the wire is not too large, one-eighth of an inch in diameter is best. The bead must fill the loop and be as clear as glass and colorless. If it is colored or not clear, heat it till it melts and throw it off; a second trial will generally give a clear and colorless bead unless the wire is very dirty. Having a good borax bead, dip it into the matter left undissolved by the hydrochloric acid, and heat it again till the bead is thoroughly melted and clear. Now look through the bead as a lens and note its color. If it is blue, cobalt is present in the precipitate. If it is brown, nickel is present and no cobalt. Should the bead be opaque there is too much precipitate in it and more borax must be melted on it to make it show the color. In the last case heat the bead till it melts, throw off part of it, and, while it is still hot, dip it again into borax and remelt it.

139. If the bead is blue from the presence of cobalt, nickel *may* be present, its brown color being covered by the blue of the first metal. In this case the two metals must be separated by the following process: Dry the precipitate as in **52** and dissolve it, in a dish, in a few drops of aqua regia, boiling off the excess of acid till only a drop remains. Take all the care prescribed in **53**, dilute the fluid in the dish with a little water and add sodium hydroxide till it is very nearly neutralized but still acid. Now add potassium nitrite (1 in 2) and acetic acid to strong acid reaction. Add the nitrite to the amount of three times the volume of the solution, hence the latter must not be too large. If it is large, evaporate it before adding the nitrite. After adding the acetic acid allow the mixture to stand twelve hours, when the cobalt will have separated as a yellow precipitate of nitrite of cobalt and potassium. Filter out the precipitate and add sodium hydroxide to the filtrate; a green precipitate, giving a brown bead with borax, indicates nickel.

140. The solution **137** which may contain the other metals of this group is now examined. As stated above, these metals are present as chlorides. In the case of iron, it is in the form of ferrous chloride, and the first step is to convert it into ferric chloride, in order to precipitate it in the coming operations. For this purpose put the solution into a dish and add a very little solid potassium chlorate. Boil the solution for some time, and, if it is cloudy, add a very little more chlorate. When finished, the fluid should be clear, and free from the odor of chlorine. Add to it, with stirring, sodium hydroxide until it is alkaline to red litmus paper. Then add *a little more* hydroxide and boil the mixture for some minutes. The precipitate contains iron, manganese and chromium as hydroxides, while zinc and aluminium go into solution, their hydroxides being soluble in the excess of sodium hydroxide used. Filter out the precipitate and wash it. Put the solution aside for the present (see **147**).

141. Dry the precipitate just obtained; when dry, or nearly so, mix it with dry sodium carbonate. This is best done by scraping the dried precipitate from the filter paper with a clean pen-knife, and rubbing it in a small porcelain dish with the sodium carbonate by means of the small end of a pestle. The mixture should be dry and nearly white; if it is a dark color more sodium carbonate must be added. If an insufficient quantity of carbonate is added the next step is not easy to perform.

142. Place the mixture just made on a piece of platinum foil held on a stick of charcoal, and by means of the blowpipe heat it until it melts. With the blowpipe blow very gently at first to avoid the scattering of the particles of the mixture. Having obtained a complete fusion of the mixture, place on one corner of it a small crystal of sodium nitrate, and heat the latter with the point of a blue blowpipe flame until it foams up, then remove the flame at once. Allow the fusion to cool. Note the color of the fusion at the point where the nitrate was fused and if it is bluish-green, it denotes the presence of manganese.

143. Having determined the presence or absence of manganese by the test with sodium nitrate just given, proceed to add more sodium nitrate to the fusion in small quantities, fusing on each addition until the entire mass has been made to foam up thoroughly. Allow the mass to cool, place it in a dish while it is still attached to the platinum, add water and heat until the mass becomes detached from the foil. Wash the foil with a little water and remove it from the dish. Boil the contents of the dish until the fusion has dissolved except perhaps some dark colored particles that readily settle. Filter out this dark material, wash it with water, preserve it (see **146**) and examine the filtrate as directed in **144** and **145**.

144. If the filtrate is yellow, add to it enough acetic acid to make it redden blue litmus paper, shaking well after adding the acid and before testing with the paper. To the acid fluid add lead acetate; a yellow precipitate is lead chromate and indicates the presence of chromium.

145. Should the filtrate from the boiling of the fusion run through the filter colorless, chromium cannot be present, as all chromates are colored; therefore the addition of acetic acid and lead acetate may be omitted.

146. The dark colored material on the filter from the fusion solution **143**, is dissolved off the paper by dropping on it a little hydrochloric acid, letting it run into a clean test-tube, in which it is heated until it is clear. Now dilute the acid solution with a little water and add to it a few drops of potassium sulphocyanide; a deep red color indicates the presence of iron. A pale orange color shows the presence of a trace of iron which will be found

in a large number of substances as an impurity. The original substance should be examined by special tests to determine if ferrous or ferric compounds are present (184).

147. We have now to examine the alkaline solution containing the aluminium and zinc. This we filtered from the precipitate **140** obtained after boiling with potassium chlorate and an excess of sodium hydroxide. This alkaline fluid is mixed with hydrochloric acid until, on shaking, it reddens blue litmus paper. It is then mixed with ammonium hydroxide until, on shaking, it smells slightly of the latter. A light flocculent precipitate of aluminium hydroxide indicates the presence of aluminium.

148. If the last precipitate is white, opaque and granular it contains zinc, and must be allowed to settle, the fluid poured off, the precipitate dissolved in a few drops of hydrochloric acid, and ammonium hydroxide added in slight excess as before; if aluminium is present a light flocculent precipitate will now form.

149. Filter out the aluminium precipitate and to the filtrate add ammonium sulphide, warming the fluid. A fine white precipitate of zinc sulphide indicates the presence of zinc in the third group. If cobalt gave a pink color to the acid in **137**, the zinc sulphide may contain cobalt sulphide and be dark colored; in this case, filter, reject filtrate, wash precipitate and treat it with dilute hydrochloric acid. To the acid filtrate thus obtained add ammonium hydroxide in excess, and then ammonium sulphide. A white precipitate is zinc sulphide.

150. The reasons for the steps taken for the separation of the metals of the third group are as follows:

The filtrate from the first group of metals is acid with hydrochloric acid used in excess to precipitate those metals. In order to obtain the metals of the third group this filtrate must be made alkaline, but before we do this, ammonium chloride is added to prevent the precipitation of magnesium hydroxide by the ammonium hydroxide, which we use to make the filtrate alkaline. As the quantity of magnesium present is unknown, we add the ammonium chloride in good quantity to be sure we have enough. The addition of the ammonium chloride does not affect the reaction of the fluid, and we must now add ammonium hydroxide until the fluid

smells of it after being well shaken. Next we add ammonium sulphide, even if the ammonium hydroxide has already given a precipitate. This precipitate that is sometimes obtained on the addition of ammonium hydroxide may be partly the hydroxides of some of the metals of the third group and partly the sulphides of the same, the latter being present from the excess of hydrogen sulphide used to precipitate the metals of the second group, and which remains in the filtrate from that group. As the appearance of the precipitate is no guide as to the amount of ammonium sulphide that is necessary to completely precipitate the metals of the third group, we add it in moderate quantity, shake the mixture well and proceed to filter. Taking the first few drops of the filtrate we add to it a drop of ammonium sulphide to see if we get a precipitate. If no precipitate is formed under these circumstances we know that the precipitation of the metals of the third group is complete; but if, on the other hand, we find that the addition of another drop of ammonium sulphide produces a precipitate, we must act as follows: Let all the fluid run through the filter paper, and also wash the latter once, spreading the water uniformly over it. Now return the few drops of filtrate that you tested with one drop of ammonium sulphide, to the bulk of the filtrate and add more ammonium sulphide. The mixture thus obtained is poured on to the filter first used and the filtrate again tested to make quite sure that enough ammonium sulphide has now been added. The ammonium sulphide turns any hydroxides present in the ammonium hydroxide precipitate into sulphides except aluminium and chromium hydroxides, which are not affected. Wash the precipitate well before proceeding further. This is necessary to prevent the metals of the fourth group interfering with the detection of those of the third. In presence of nickel, and if a large excess of ammonium sulphide has been used, the filtrate is brown colored but clear.

151. The first step in the treatment of the precipitate is for the purpose of separating the sulphides of cobalt and nickel from the rest of the sulphides and hydroxides in the group. That this separation may be perfect, the precipitate must be in the moist condition, as just precipitated. If it is dry, it may be that some of the sulphides or hydroxides will not dissolve in hydrochloric acid and thus remain with the sulphides of cobalt and nickel. Another

important point is that the acid used should not be too strong, as in this case some of the nickel and cobalt sulphides may then pass into solution. We will now notice the matter insoluble in hydrochloric acid.

152. The test with the borax bead will show at once whether cobalt is present; but care must be taken that the bead first formed on the platinum wire is clear and colorless like glass. The presence of cobalt masks, by its color, the presence of nickel in the borax bead, therefore we have to separate the former before we can detect the latter. The separation of the two metals depends on the formation of the nitrite of cobalt and potassium in an acetic acid solution of the metal. Under the same circumstances nickel does not give any precipitate, but it is precipitated from the filtrate as nickel hydroxide on the addition of potassium hydroxide in excess. The presence of nickel in this last precipitate is confirmed by the brown bead which it gives with borax. The cobalt precipitate may also be tested in the same way, giving a blue bead, but if found at first in the sulphides insoluble in hydrochloric acid, this proceeding is unnecessary.

153. If a brown bead is obtained with the original sulphides insoluble in hydrochloric acid, the separation of the cobalt by nitrite becomes unnecessary.

154. We will now discuss the reasons for the course of procedure with the solution obtained from treatment of the original sulphides with hydrochloric acid.

In this case we have a fluid containing the hydrochloric acid which we used in excess, also some hydrogen sulphide, together with the chlorides of the metals of the third group the sulphides of which are soluble in hydrochloric acid. The iron chloride in this solution is in such a condition that it is not readily precipitated in the future; it is in the ferrous condition, and, in order to precipitate it, it must be changed to the ferric state. To accomplish this, we put into the fluid some potassium chlorate, and only so much as will just complete the change and no more. That we have enough is known by the change in the fluid, which first becomes milky, and, as the change is completed, clears up. If iron is present, we also note another change; the fluid turns from colorless to yellow or brown, according to the amount of the metal

present. Boiling the fluid is for the purpose of driving off the chlorine compounds formed in the solution by the action of the potassium chlorate on the hydrochloric acid in it. These would interfere with the precipitation of the metals in the future. The next step is to add enough sodium hydroxide not only to precipitate the iron, chromium and manganese as hydroxides, but also to hold the aluminium and zinc in solution. The hydroxides of iron, chromium and manganese are insoluble in sodium hydroxide, while the hydroxides of aluminium and zinc are soluble. We will now discuss the reasons for the procedure with the precipitate.

155. Having washed the precipitate and dried it, it is heated with a mixture of sodium carbonate and nitrate. This step is for the purpose of converting the chromium and manganese hydroxides into chromate and manganate of sodium. The first of these is yellow; the latter is bluish-green, and the depth of this last color is so great that the mass may appear black if much manganese is present; this is the reason that only a small portion of the sodium nitrate is added at first to give a small depth of color. But a further addition of nitrate is necessary in order to completely convert the chromium into sodium chromate for its detection. Boiling the fused mass with water decomposes the sodium manganate and leaves the sodium chromate unchanged; the sodium manganate decomposes into manganese dioxide, which remains insoluble with the iron, the latter being unchanged by the fusion and boiling. In case chromium is present the fluid will be yellow from the sodium chromate, but to make sure of the presence of chromium, acetic acid is added to the fluid until it is acid and then plumbic acetate, which should give a bright yellow precipitate of plumbic chromate. The matter insoluble after boiling the fused mass with water contains both manganese and iron, but as we have already tested for the former, it only remains to test for the latter, which we do by dissolving the insoluble matter in hydrochloric acid, boiling to expell chlorine formed by the action of the acid on the manganese dioxide present, and then adding potassium sulphocyanide. Here it should be remembered that the test for iron is an extremely delicate one, and a small change of color indicates only a trace of iron which is found in almost everything used in the laboratory.

156. We now come to the alkaline fluid containing the aluminium and zinc hydroxides. To overcome the solvent action of the sodium hydroxide we have used, we add hydrochloric acid in excess to this fluid and then an excess of ammonium hydroxide very carefully, to precipitate the aluminium as a hydroxide. In doing this in cases where much zinc is present, we often get a precipitate of a different character from that obtained with aluminium; but a very slight acquaintance with the appearance of the two hydroxides will soon serve to distinguish them. If the precipitate obtained with ammonium hydroxide is opaque and granular it probably contains zinc; in this case make the fluid acid again with hydrochloric acid, then add ammonium hydroxide in excess, when the flocculent and light precipitate of aluminium hydroxide will appear if that metal is present. The addition of ammonium sulphide to the filtrate from the aluminium hydroxide, or to the ammoniacal fluid if aluminium is absent, will give a white precipitate of zinc sulphide if that metal is present. In this case the color of the precipitate is very characteristic. It is also important to give the precipitate time to form if only small quantities of zinc are present; slight warming of the fluid also aids the formation of zinc sulphide.

The preceding methods are tabulated in the following scheme:

TABLE III. (NH₄)₂S Group.

Treat with HCl dilute (1 in 3), filter and wash.

<p>Insoluble.—Test in Borax bead. Blue bead indicates Co. Brown bead indicates Ni. If bead is blue Ni may also be present. Separate Ni & Co as per 139</p>	<p>Filtrate.—Boil in a dish with a <i>small crystal</i> of KClO₃, continue boiling till Cl is gone. Add NaOH till strongly alkaline, boil again, filter and wash well.</p> <p>Ppt.—Dry, fuse with Na₂CO₃ and NaNO₃. A green mass indicates Mn. Boil mass with water, filter and wash.</p>	<p>Insoluble.— Dissolve in HCl, boil, dilute and add KCNS. Blood red color indicates Fe.</p>	<p>Filtrate. 1. Is colorless, indicates absence of Cr. Reject. 2. Is yellow. Add Acetic Acid in excess and then Plumbic Acetate. Yellow ppt. indicates Cr.</p>	<p>Ppt.— Light and flocculent is Al. (OH)₃, and indicates Al. If granular and white dissolve in HCl, dilute solution, and add slight excess of NH₄OH. Ppt. as above indicates Al.</p>	<p>Filtrate.— Add (NH₄)₂S, white ppt. is Zn S and indicates Zn.</p>
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CHAPTER VII.

SPECIAL TESTS FOR THE METALS OF THE THIRD GROUP.

NICKEL.

Blowpipe Test.

157. In a borax bead nickel compounds give a seal brown color to the glass when the bead is cold.

Solution Tests.

158. Hydrochloric acid does not precipitate nickel solutions.

159. Hydrogen sulphide does not precipitate acid nickel solutions, but in alkaline solutions a precipitate of nickel sulphide NiS is formed.

160. Ammonium sulphide precipitates alkaline nickel solutions, giving black nickel sulphide NiS . Presence of ammonium hydroxide assists the precipitation, also the presence of ammonium chloride. Nickel sulphide is slightly soluble in ammonium sulphide, hence the filtrate from the precipitate is often brown, especially if much ammonium sulphide is used in excess. Nickel sulphide is practically insoluble in dilute hydrochloric acid, also in acetic acid, but it dissolves in warm aqua regia.

161. Sodium and potassium hydroxides precipitate nickel solutions, giving apple-green nickel hydroxide Ni(OH)_2 . The precipitate is soluble in ammonium carbonate, giving a blue fluid.

162. Ammonium hydroxide, if only a few drops are added to nickel solutions which are free from ammonium salts and neutral, gives a slight precipitate of nickel hydroxide which dissolves in excess of the precipitant to a blue fluid. Sodium and potassium hydroxides precipitate the ammoniacal solution thus formed.

163. Alkaline carbonates (of K, Na but not NH_4), give green precipitates of nickel carbonate mixed with hydroxide.

164. Potassium ferrocyanide precipitates greenish-white nickel ferrocyanide $\text{Ni}_2\text{Fe}(\text{CN})_6$, which is insoluble in hydrochloric acid.

165. Potassium ferricyanide precipitates yellowish-brown nickel ferricyanide $\text{Ni}_3\text{Fe}_2(\text{CN})_{13}$, which is insoluble in hydrochloric acid.

166. Potassium cyanide precipitates yellowish-green nickel cyanide $\text{Ni}(\text{CN})_2$, which is soluble in an excess of the precipitant. The cyanide solution of nickel thus obtained is reprecipitated by adding hydrochloric acid, giving nickel cyanide again.

167. Bromine water or solution of sodium hypochlorite added to a solution of nickel cyanide in potassium cyanide, that is slightly acid with hydrochloric acid (liberating hydrocyanic acid) and has been boiled, produce a precipitate of nickel hydroxide $\text{Ni}_2(\text{OH})_6$ on again boiling the mixture.

168. Potassium nitrite in presence of acetic acid does not precipitate nickel solutions.

169. Commercial Nickel Compounds :

Alloys :

German silver (Copper 100, Zinc 16, Nickel 40 parts).

Nickel coins (Copper, Zinc and Nickel ; or Copper and Nickel).

Salts :

Double sulphate of nickel and ammonium $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 + 6\text{H}_2\text{O}$.

Nickel sulphate.

Nickel chloride.

COBALT.

Blowpipe Tests.

170. In a borax bead, cobalt compounds give an intense blue glass.

Solution Tests.

171. Hydrochloric acid does not precipitate cobalt solutions.

172. Hydrogen sulphide does not precipitate acid cobalt solutions, but in alkaline solutions a black precipitate of cobalt sulphide CoS is formed.

173. Ammonium sulphide precipitates black cobalt sulphide CoS . Ammonium chloride aids the precipitation. The precipitate

is insoluble in dilute hydrochloric acid, also acetic acid, but dissolves in warm aqua regia.

174. Sodium and potassium hydroxides precipitate basic cobalt hydroxide of various colors, from dirty green when cold to pale red when hot, and its composition is variable; the red precipitate is $\text{Co}(\text{OH})_2$. Ammonium chloride retards or prevents the precipitation.

175. Ammonium hydroxide, if used in small quantity, gives the same precipitate as the foregoing, but it is soluble in excess of the reagent, forming a red fluid. Presence of acid or of ammonium salts prevents the precipitation with ammonium hydroxide. Sodium and potassium hydroxides precipitate the ammoniacal solution thus formed.

176. Alkaline carbonates (of Na, K but not NH_4) give pink precipitates of cobalt carbonate mixed with hydroxide.

177. Potassium ferrocyanide precipitates green cobalt ferrocyanide $\text{Co}_3\text{Fe}(\text{CN})_6$, which is insoluble in hydrochloric acid.

178. Potassium ferricyanide precipitates brownish-red cobalt ferricyanide $\text{Co}_3\text{Fe}_3(\text{CN})_{12}$, which is insoluble in hydrochloric acid.

179. Potassium cyanide precipitates brownish-white cobalt cyanide $\text{Co}(\text{CN})_2$, which is soluble in excess of the precipitant. Hydrochloric acid precipitates the cyanide solution, giving cobalt cyanide again.

180. Bromine water or sodium hypochlorite added to a solution of cobalt cyanide in potassium cyanide, that is slightly acid with hydrochloric acid (liberating hydrocyanic acid), and has been boiled, do not produce any precipitate. Hydrochloric acid also fails to precipitate the acid, boiled solution of cobalt cyanide in potassium cyanide.

181. Potassium nitrite, in presence of acetic acid, precipitates cobalt potassium nitrite as a fine crystalline powder $\text{K}_6\text{Co}_2(\text{NO}_2)_{12} + 3\text{H}_2\text{O}$. The precipitate is decidedly soluble in water, but insoluble in presence of potassium nitrite. A solution of the precipitate in boiling water gives cobalt hydroxide on addition of potassium hydroxide.

182. Commercial Cobalt Compounds:

Smalt is silicate of cobalt and potassium.

Zaffre is also a crude silicate of cobalt made by heating cobalt ore with sand.

Thenard's blue is phosphate of cobalt and aluminium.

Cobalt ultramarine is another name for Thenard's blue.

Rinnmann's green is a mixture of zinc and cobalt oxides.

Sympathetic ink is a solution of cobalt chloride.

Black oxide of cobalt is Co_2O_3 .

Cobalt sulphate.

Cobalt chloride.

Cobalt nitrate.

IRON.**Blowpipe Test.**

183. In a borax bead, iron gives a color to the glass that varies from a yellow while hot, to brownish-yellow when cold. In the inner flame the glass becomes nearly colorless while hot and bottle green when cold.

Solution Tests.

184. There are two classes of iron salts that may occur in solution. One of these is the ferrous class, giving pale green solutions, the other is the ferric class which gives yellow or brown solutions.

Ferrous Solutions.

185. Hydrochloric acid does not affect these solutions.

186. Hydrogen sulphide does not affect these solutions if they are acid, but in alkaline solutions (with organic matter) it gives black ferrous sulphide FeS .

187. Ammonium sulphide precipitates black ferrous sulphide FeS , which is insoluble in alkaline hydroxides and sulphides, and soluble in dilute hydrochloric acid, also in nitric and acetic acids. Ammonium chloride assists the precipitation.

188. Alkaline hydroxides (of K , Na and NH_4), give a precipitate of ferrous hydroxide, $\text{Fe}(\text{OH})_2$, that varies in color from white to dirty green or brown after its exposure to the air. Ammonium salts prevent the precipitation by ammonium hydroxide, and

partially with potassium hydroxide. Organic acids, sugar and like organic matters, retard or prevent the precipitation of ferrous hydroxide.

189. Alkaline carbonates give a white precipitate of ferrous carbonate FeCO_3 , which gets dirty green on exposure to the air, and soon changes to brown ferric hydroxide.

190. Potassium ferrocyanide gives a precipitate of potassium ferrous ferrocyanide $\text{K}_2\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, which becomes Prussian blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ on exposure to the air. Nitric acid likewise converts it into ferric ferrocyanide (Prussian blue).

191. Potassium ferricyanide precipitates blue ferrous ferricyanide $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, which has the same color as Prussian blue. The precipitate is insoluble in hydrochloric acid, but is decomposed by alkaline hydroxides.

192. Potassium sulphocyanide does not affect ferrous solutions.

193. Barium carbonate does not precipitate these solutions.

Ferric Solutions.

194. Hydrochloric acid does not affect these solutions.

195. Hydrogen sulphide gives a milky precipitate of sulphur in acid ferric solutions and at the same time converts them into ferrous solutions. In alkaline solutions (*e. g.*, those containing organic matter), a precipitate of ferrous sulphide FeS is formed, mixed with sulphur.

196. Ammonium sulphide gives a precipitate of ferrous sulphide FeS mixed with sulphur. Ammonium chloride assists the precipitation. The precipitate is insoluble in alkaline hydroxides and sulphides, but dissolves in dilute hydrochloric acid.

197. Alkaline hydroxides (of K , Na and NH_4) give a precipitate of ferric hydroxide $\text{Fe}_2(\text{OH})_6$, which is insoluble in ammonium salts and also in excess of the precipitant. Organic matters prevent this precipitation.

198. Alkaline carbonates give a precipitate of ferric hydroxide, with the escape of carbon dioxide as a gas.

199. Potassium ferrocyanide precipitates ferric ferrocyanide $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ or Prussian blue, which is insoluble in hydrochloric acid, but is decomposed by alkaline hydroxides.

200. Potassium ferricyanide does not precipitate ferric solutions, but deepens their color.

201. Potassium sulphocyanide gives a blood-red color with ferric solutions. The test is extremely delicate, and may be made still more so by adding hydrochloric acid to the solution and shaking with ether, in which the red color dissolves.

202. Barium carbonate precipitates basic ferric hydroxide, with escape of carbon dioxide as a gas.

203. Commercial Iron Compounds :

Pig iron is iron with carbon, silicon, phosphorus and sulphur as impurities.

Wrought or bar iron is nearly pure, but contains traces of the same impurities as pig iron.

Steel is the same as wrought iron with more or less carbon.

Spiegel-Eisen is an alloy of iron and manganese.

Ferrum reductum is metallic iron reduced by hydrogen from powdered ferric oxide.

Ochre is ferric oxide with more or less clay according to color.

Iron ore may be magnetite Fe_3O_4 , hematite Fe_2O_3 , or spathic iron (a basic carbonate).

Copperas is ferrous sulphate $(\text{FeSO}_4) + 7\text{H}_2\text{O}$.

Green vitriol is the same as preceding.

Both of these are often called "iron sulphate" or protosulphate.

Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

Liquor ferri chloridi contains ferric chloride.

Liquor ferri persulphatis contains ferric sulphate.

Iron scale preparations of U. S. P. contain ferric compounds.

Iron hypophosphite of U. S. P. is the ferric compound.

Iron pyrophosphate of U. S. P. is the ferric compound rendered soluble by sodium citrate.

Saccharated carbonate of iron of U. S. P. contains the ferrous compound.

Ammonia iron alum of U. S. P. contains the ferric compound.

Saccharated iodide of iron of U. S. P. contains the ferrous compound.

Lactate of iron of U. S. P. contains the ferrous compound.

Oxalate of iron of U. S. P. contains the ferrous compound.

Valerianate of iron of U. S. P. contains the ferric compound.

MANGANESE.

Blowpipe Tests.

204. In a borax bead, manganese gives an amethyst color to the glass. In the inner blowpipe flame the bead will become colorless.

205. Heated with sodium carbonate on platinum foil, manganese gives a green color to the mass, which is more apparent if a little sodium nitrate is used with it.

Solution Tests.

206. Hydrochloric acid does not affect manganese solutions.

207. Hydrogen sulphide does not affect acid solutions of manganese, but in alkaline solutions it precipitates manganese sulphide MnS .

208. Ammonium sulphide precipitates manganese sulphide MnS , which is flesh colored. The precipitate turns brown in the air; it is insoluble in ammonium sulphide and alkaline hydroxides. It dissolves in hydrochloric, nitric and acetic acids. Ammonium chloride assists the precipitation by ammonium sulphide.

209. Sodium and potassium hydroxides precipitate white manganese hydroxide $Mn(OH)_2$, which turns brown in the air.

210. Ammonium hydroxide produces the same precipitate as in the preceding case. Presence of ammonium chloride prevents the precipitation.

211. Alkaline carbonates precipitate manganese carbonate $MnCO_3$, or a mixture of carbonate and hydroxide. Ammonium carbonate precipitates the manganese completely as pure carbonate even in presence of ammonium chloride. Organic matter interferes with the precipitation by alkaline carbonates.

212. Bromine water or sodium hypochlorite added to a manganese solution containing an excess of sodium or potassium hydroxide or acetate, produce a precipitate of manganese dioxide when the mixture is heated.

213. Potassium ferrocyanide precipitates reddish-white manganese ferrocyanide $\text{Mn}_2\text{Fe}(\text{CN})_6$, which is soluble in hydrochloric acid.

214. Potassium ferricyanide precipitates brown manganese ferricyanide $\text{Mn}_3[\text{Fe}(\text{CN})_6]_2$, which is insoluble in hydrochloric acid, or ammonium hydroxide.

215. Barium carbonate does not precipitate manganese solutions. Manganese sulphate is an exception; this forms barium sulphate and manganese hydroxide, while carbon dioxide escapes.

216. Commercial Manganese Compounds :

Spiegel-Eisen is an alloy of manganese and iron.

Ferro-manganese is practically another variety of spiegel-eisen.

Black oxide of manganese is the dioxide of the metal; it is often called peroxide of manganese and sometimes "manganese".

Condy's green disinfectant is sodium manganate Na_2MnO_4 .

Condy's red disinfectant is potassium permanganate $\text{K}_2\text{Mn}_2\text{O}_8$.

Manganous sulphate.

Manganous chloride.

CHROMIUM.

Blowpipe Tests.

217. In a borax bead, chromium compounds color the glass green, which is best seen when cold.

218. Chromium compounds, heated with sodium carbonate and nitrate upon platinum foil, produce a yellow mass, which dissolves in water on boiling, giving a yellow solution.

Solution Tests.

219. Hydrochloric acid does not affect solutions of chromium compounds.

220. Hydrogen sulphide does not affect these solutions.

221. Ammonium hydroxide precipitates green or bluish chromium hydroxide $\text{Cr}_2(\text{O H})_6$, which is somewhat soluble in an

excess of the precipitant in the cold ; boiling completes the precipitation. The precipitate is soluble in hydrochloric acid.

222. Ammonium sulphide precipitates green or bluish chromium hydroxide $\text{Cr}_2(\text{OH})_6$, hydrogen sulphide escaping.

223. Sodium and potassium hydroxides precipitate bluish-green chromium hydroxide, which is soluble in an excess of the precipitant. Long boiling precipitates the alkaline solutions, or addition of ammonium chloride will produce the same result.

224. Alkaline carbonates precipitate basic chromium carbonate, which is slightly soluble in a large excess of the precipitant. It is soluble in hydrochloric acid.

225. Barium carbonate precipitates basic green chromium hydroxide, but completely only after long standing.

226. N. B.—Organic matters interfere with the action of hydroxides and carbonates.

227. Bromine water or sodium hypochlorite added to chromium solution containing an excess of sodium or potassium hydroxide, and if the mixture boiled, the chromium is converted into chromic acid and colors the fluid yellow.

228. Commercial Chromium Compounds :

Chrome yellow is lead chromate.

Chrome orange is basic lead chromate.

Bichromate of potassium is $\text{K}_2\text{Cr}_2\text{O}_7$; it is also called Dichromate.

Chrome green is chromium oxide, Cr_2O_3 .

ZINC.

229. Blowpipe tests are of little value.

Solution Tests.

230. Hydrochloric acid does not affect zinc solutions.

231. Hydrogen sulphide does not affect acid zinc solutions, but in alkaline solutions it precipitates white zinc sulphide ZnS . In presence of organic acids (*e. g.*, acetic) zinc sulphide is also formed.

232. Ammonium sulphide precipitates white zinc sulphide ZnS . Ammonium chloride promotes the precipitation. The precipitate is insoluble in ammonium sulphide and alkaline hydroxides; it is soluble in hydrochloric, nitric and sulphuric acids, but is insoluble in acetic acid.

233. Sodium and potassium hydroxides precipitate white zinc hydroxide Zn(OH)_2 . The precipitate is soluble in an excess of the reagent. Boiling these solutions will precipitate them if they are dilute, but solutions strong in alkaline hydroxide are not precipitated.

234. Ammonium hydroxide added in small quantity to solutions of zinc gives zinc hydroxide as a precipitate, which is readily soluble in an excess of the precipitant. Ammonium salts interfere with the precipitation. Boiling the diluted solution in ammonium hydroxide precipitates the zinc as hydroxide, but not in presence of ammonium salts.

235. Sodium and potassium carbonates give a white precipitate of basic zinc carbonate, which is insoluble in an excess of the precipitant. Ammonium salts interfere with the precipitation.

236. Ammonium carbonate precipitates white basic zinc carbonate, which is soluble in an excess of the precipitant. Boiling the diluted solution in ammonium carbonate precipitates the zinc carbonate again. Ammonium salts interfere with this result.

237. N. B.—Organic matters interfere with the precipitation of the hydroxide and basic carbonate of zinc.

238. Barium carbonate does not precipitate zinc solutions. Zinc sulphate is an exception.

239. Potassium ferrocyanide gives zinc ferrocyanide $\text{Zn}_2\text{Fe(CN)}_6$ as a slimy white precipitate. It is slightly soluble in an excess of the precipitant, but insoluble in hydrochloric acid.

240. Potassium ferricyanide precipitates brownish-yellow zinc ferricyanide $\text{Zn}_3[\text{Fe(CN)}_6]_2$, which is soluble in hydrochloric acid and ammonium hydroxide.

241. Commercial Zinc Compounds :

Spelter is metallic zinc.

Galvanized iron is sheet iron coated with zinc.

"Zinc" is the name often given to the calcined oxide of zinc.

Zinc white is the same as the preceding.

White vitriol is zinc sulphate.

Colorless disinfecting fluids are usually zinc chloride mixed with other chlorides such as salt.

ALUMINIUM.

Blowpipe Test.

242. Heated on charcoal, aluminium compounds give white aluminium oxide, which, on being moistened with cobalt chloride solution and again strongly heated, gives a fine blue mass.

Solution Tests.

243. Hydrochloric acid does not affect aluminium solutions.

244. Hydrogen sulphide does not affect acid aluminium solutions.

245. Sodium and potassium hydroxides precipitate white flocculent aluminium hydroxide $\text{Al}_2(\text{OH})_6$, which is soluble in an excess of the precipitant. Boiling does not cause a precipitate in the solutions, but ammonium chloride throws down aluminium hydroxide in them, especially if heated.

246. Ammonium hydroxide precipitates aluminium hydroxide, which is slightly soluble in a large excess of the precipitant. Ammonium salts lessen the solubility. Boiling assists the precipitation.

247. Ammonium sulphide produces the same precipitate as ammonium hydroxide, hydrogen sulphide escaping.

248. Alkaline carbonates (of K, Na and NH_4) precipitate white basic aluminium carbonate. The precipitates with potassium or sodium carbonates are soluble in an excess of the latter; but those produced by ammonium carbonate only slightly, boiling promoting the reprecipitation by the latter.

249. Barium carbonate precipitates basic aluminium hydroxide, even in the cold.

250. Hydro-disodic phosphate precipitates white bulky aluminium phosphate AlPO_4 . The precipitate is soluble in sodium

and potassium hydroxides, but only very slightly in ammonium hydroxide. Ammonium salts decrease its solubility in ammonium hydroxide. Ammonium chloride precipitates the phosphate from its solution in sodium or potassium hydroxide. Aluminium phosphate is soluble in hydrochloric and nitric acids, but not in acetic acid.

251. Commercial Aluminium Compounds:

Aluminium bronze contains 10% of aluminium.

Alum is a double sulphate of aluminium and ammonium or potassium.

Alumina is pure clay or aluminium silicate.

Alumazuli.

Ultramarine.

Sapphire.

Ruby.

Mica.

Aluminium acetate.

Aluminium sulphate.

CHAPTER VIII.

SEPARATION OF THE METALS OF THE FOURTH GROUP.

252. As in the previous group, the precipitate must be well washed. Prepare some dilute hydrochloric acid (1 of acid to 2 of water), and pour it upon the filter holding the precipitate of the fourth group. The quantity of acid used will depend on the amount of precipitate, but one-third of a test-tube full will usually be sufficient. Hold the funnel over a porcelain dish that is going to be used for the evaporation, which follows. If the first passage of the acid through the funnel does not dissolve the whole of the precipitate, return the fluid that has run through into the dish back to the filter paper again. A second transfer of this kind will usually dissolve the entire precipitate.

253. The fluid just obtained is now evaporated to dryness very carefully. To do this the flame under the dish should be a small one, and its point just touch the dish, and, as the fluid evaporates, the dish should be moved around, so that the contents are kept constantly spread over the surface. These precautions are necessary to avoid overheating the solid matter during the evaporation. In fact, the success of the following operations depends upon this first step in the separation of the metals of this group. The greatest possible care is also essential to prevent the sides of the dish that are covered with solid residue from being overheated; hence a very small flame is used.

254. Having driven off all the fluid at a gentle heat, allow the dish to cool thoroughly. Now add to the residue in the dish enough alcohol to make it fluid enough to filter, and no more; in other words keep the bulk of the fluid down. Grind the contents of the dish with a small pestle or flattened end of a glass rod until the alcohol has been very intimately mixed with the residue. Allow the insoluble matter, if any, to settle, pour off the fluid through a small filter that has been moistened with *alcohol*, not water, into a clean test-tube. Put upon the insoluble matter in the dish another quantity of alcohol equal to twice the first used, grind it with the residue again, and pour it through the same filter paper

used previously. The insoluble matter is barium chloride and is treated as follows :

255. The residue in the dish or the insoluble matter on the filter paper is treated with water, and the solution filtered into a clean test-tube. This solution is divided into several parts. To one portion add one drop of sulphuric acid ; a heavy white precipitate which is insoluble in hydrochloric acid indicates the presence of barium. To confirm this test, dip a clean platinum wire into some of the water solution, and heat it in the flame of a Bunsen burner ; a green flame indicates barium. The cleaning of the platinum wire is a very important matter or the color of the flame will be of no value. To clean such a wire, place a few drops of hydrochloric acid in a watch-glass, heat the wire red hot and plunge it into the acid, repeating the operation till the wire will not color the flame when heated in it.

As a still further proof of the presence of barium, the water solution of barium chloride may be tested with a drop or two of potassium dichromate, when a yellow precipitate indicates barium.

256. We now take up the alcoholic solution obtained by treating the residue in the dish. To this we add sulphuric acid (10 drops will do), shake the mixture well and filter. The acid precipitates strontium and calcium, and the filtrate may be rejected, as it contains nothing that we want. Drain the precipitate from the fluid that adheres to it, break a hole through the filter paper with a glass rod, and wash the precipitate into a clean test-tube with as little water as possible. In another test-tube make a solution of ammonium sulphate by taking forty drops of sulphuric acid, four times the volume of water, and adding to this mixture ammonium hydroxide till it smells strongly of the latter. Shake the mixture thoroughly well as the ammonium hydroxide is added, and at last add to the mixture one-fourth of its volume more of ammonium hydroxide. The fluid so prepared is now put upon the precipitate obtained with sulphuric acid, from the alcoholic solution above. Boil the precipitate with the ammonium sulphate solution for some minutes, taking care not to make it boil over. A gentle boiling is all that is needed. Filter out the insoluble matter.

257. The sulphate insoluble in the ammonium sulphate contains strontium if present, and its presence may be detected by

heating some of the precipitate, moistened with hydrochloric acid, on a platinum wire in a Bunsen flame. The same care about a clean wire is necessary here as was in the case of barium. It is also necessary to know the color of the flame given by strontium. It is of a bright red tint, and this is brought out by the use of hydrochloric acid on the wire with the precipitate. Calcium gives a flame that is very much like that of strontium, but yellowish-red; a little experience with the two will soon serve to tell the difference.

258. In the filtrate from the sulphates boiled with ammonium sulphate we test for calcium by adding ammonium oxalate. A fine white precipitate indicates the presence of calcium. The only precaution necessary here is that the fluid must be made alkaline with excess of ammonium hydroxide.

The reasons for the various operations for the separation of the metals of the fourth group are as follows:

259. The precipitate obtained on adding ammonium carbonate to the filtrate from the third group of metals consists of the carbonates of barium, strontium and calcium. The presence of ammonium chloride in the fluid serves here also, as in the third group, to prevent the precipitation of magnesium carbonate by ammonium carbonate. The fluid also contains ammonium hydroxide in excess, as this is essential to the precipitation of the barium, strontium and calcium as carbonates by ammonium carbonate.

260. The precipitate, deprived by washing of any metals of the fifth group, is treated with hydrochloric acid, and the carbonates become chlorides of barium, strontium and calcium. These chlorides in solution are obtained in a dry condition by evaporation of the fluid, and great care should be taken that they remain as chlorides throughout this operation. The danger is in overheating them as they dry on the sides of the dish. If they are overheated they become oxides of the metals of the fourth group and do not respond to the treatment for their separation.

261. The dry chlorides must be allowed to cool or the alcohol will evaporate if it is placed in the hot dish. The treatment with alcohol gives a solution of the strontium and calcium chlorides, which are soluble in it, while the barium chloride remains behind, insoluble. Hence it is important that all the metals should be in

the residue as chlorides and not oxides, which latter are not soluble in alcohol.

262. The barium chloride is insoluble in alcohol, but it is readily soluble in water. The precipitate obtained with sulphuric acid in the water solution is barium sulphate, which is insoluble in hydrochloric acid. The yellow precipitate obtained with potassium dichromate is barium chromate.

263. In the filtrate containing the chlorides of strontium and calcium in alcohol, we precipitate both metals as sulphates when we add sulphuric acid. As this precipitation of the sulphates is complete, the fluid contains nothing except an excess of sulphuric acid, alcohol and water. The precipitated sulphates are boiled with ammonium sulphate and ammonium hydroxide, a mixture that has the power of dissolving out the calcium sulphate, leaving the strontium sulphate insoluble. The calcium sulphate is not very soluble in the ammoniacal mixture; it is therefore not necessary to boil until the solution clears, even if only calcium sulphate is present. Hence a precipitate of calcium sulphate may be obtained which will not entirely dissolve in the ammonium sulphate, and the beginner may think it is strontium sulphate that he has on the filter paper, when it is only some of the calcium sulphate which the ammonium sulphate solution has not dissolved because of an insufficiency of the latter. But there is always enough of the calcium sulphate that goes into solution to give the test for calcium if that metal is present.

264. The filtrate from the insoluble sulphates, which must be alkaline, is mixed with ammonium oxalate, which gives a precipitate of calcium oxalate if calcium is present; a very characteristic test for this metal. The precipitate is fine and white. It is insoluble in acetic acid, but dissolves in hydrochloric acid.

265. In testing the precipitate of sulphate upon the filter paper, the only thing to remember is that it may contain both calcium sulphate with strontium sulphate, unless the first is present in very moderate quantities, and this calcium sulphate gives an orange-red flame when heated on the platinum wire. But a little experience will soon show the difference between the two colors. Special tests for strontium are also made in cases of doubt. (See **279** *et seq.*)

The operations described above are tabulated in the following scheme:

TABLE IV. $(\text{NH}_4)_2\text{CO}_3$ Group.

Dissolve in HCl (1 in 3), evaporate to dryness, *don't overheat*. Allow to cool, add alcohol, grind up with pestle, pour off, and repeat treatment with alcohol, filter and wash with alcohol. *Moisten filter paper with alcohol, not water.*

<p>Insoluble—Dissolve in water and add H_2SO_4. A white ppt. is BaSO_4 and indicates Ba. Also test in flame.</p>	<p>Filtrate.—Add H_2SO_4, shake well, filter and wash. <i>Reject filtrate.</i> Ppt.—Boil with $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{OH}$ for some minutes and filter.</p> <p>Ppt.—Test on Pt wire in Bunsen flame. Red flame indicates Sr.</p> <p>Filtrate.—Add $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Fine white ppt. indicates Ca.</p>
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CHAPTER IX.

SPECIAL TESTS FOR THE METALS OF THE FOURTH GROUP.

BARIUM.

Blowpipe Test.

266. In the flame barium compounds give a yellowish-green color.

Solution Tests.

267. Hydrochloric acid added to barium solutions in small quantity does not affect them, but if the acid is strong and is added in large quantity it produces a white precipitate of barium chloride. This precipitation is due to the fact that barium chloride is soluble in water but not in hydrochloric acid. Addition of water to the fluid containing the barium chloride precipitate dissolves the latter, especially on warming.

268. Nitric acid produces the same kind of result as hydrochloric acid in barium solutions, the barium nitrate formed dissolving in an excess of water.

269. Ammonium hydroxide produces no precipitate in barium solutions, if the hydroxide is free from carbonate.

270. Sodium and potassium hydroxides do not precipitate dilute barium solutions, but in strong solutions they give a white precipitate of barium hydroxide $\text{Ba}(\text{OH})_2$, which is soluble on adding water.

271. Alkaline carbonates (of K, Na and NH_4) give a white precipitate of barium carbonate BaCO_3 , which is slightly soluble in ammonium chloride. In acid barium solutions the precipitation is incomplete, even with excess of carbonate, until the fluid is boiled; this expels carbon dioxide which retains barium carbonate in solution.

272. Sulphuric acid and soluble sulphates give a white precipitate of barium sulphate BaSO_4 , which is insoluble in al-

kalies and dilute acids, but dissolves slightly in strong acids, and in strong solutions of ammonium salts not containing sulphuric acid or a sulphate.

273. Calcium sulphate yields barium sulphate, even in very dilute solutions.

274. Hydrofluosilicic acid gives barium silicofluoride BaSiF_6 , as a colorless, crystalline precipitate, which separates best on adding to the fluid an equal volume of alcohol. It is slightly soluble in nitric and hydrochloric acids. The test is a very delicate one.

275. Sodium phosphate gives barium phosphate BaHPO_4 , as a white precipitate, which is soluble in acids. It is slightly soluble in ammonium chloride.

276. Ammonium oxalate gives white barium oxalate BaC_2O_4 , which is soluble in nitric and hydrochloric acids. It is insoluble in acetic or oxalic acid unless just precipitated. Both the acetic and oxalic acid solution quickly deposits acid barium oxalate $\text{BaH}_2(\text{C}_2\text{O}_4)_2$ as a crystalline powder.

277. Potassium chromate and dichromate give yellow barium chromate BaCrO_4 even in dilute solutions. It is soluble in nitric and hydrochloric acids, but insoluble in chromic and acetic acids.

278. Commercial Barium Compounds :

Barytes is barium sulphate found in nature.

Permanent white is barium sulphate.

Green fire is made with barium nitrate.

Natural barium carbonate (witherite) is said to be used for rat poison.

Barium chloride.

STRONTIUM.

Blowpipe Test.

279. In the flame strontium compounds give a scarlet-red color. If the color is seen through blue glass it appears of a rose-pink tint.

Solution Tests.

280. Hydrochloric acid does not affect strontium solutions even if the acid is strong and in large excess.

281. Nitric acid behaves like hydrochloric acid.

282. Ammonium hydroxide gives no precipitate if the hydroxide is free from carbonate.

283. Sodium and potassium hydroxides behave very much the same as with barium solutions.

284. Alkaline carbonates (of K, Na and NH_4) give a white precipitate of strontium carbonate SrCO_3 . It is soluble in dilute acids. If the alkaline carbonate is added to an acid solution the precipitation is only complete after boiling. The precipitate is very slightly soluble in ammonium chloride.

285. Sulphuric acid and soluble sulphates give white strontium sulphate, SrSO_4 . Heat assists precipitation. Addition of alcohol to the fluid assists precipitation in the cold. The precipitate is somewhat soluble in water; also in nitric and hydrochloric acids. It is insoluble in ammonium sulphate solution.

286. Calcium sulphate produces the same precipitate as the preceding. In this case the precipitation takes some time.

287. Hydrofluosilicic acid does not precipitate strontium solutions, not even on the addition of alcohol, unless they are concentrated.

288. Sodium phosphate gives white strontium phosphate SrHPO_4 , which is soluble in dilute acids. The precipitate is slightly soluble in ammonium chloride.

289. Ammonium oxalate gives white strontium oxalate SrC_2O_4 , which is soluble in nitric and hydrochloric acid. If just precipitated it is soluble in oxalic or acetic acid. These solutions afterward deposit acid strontium oxalate $\text{SrH}_2(\text{C}_2\text{O}_4)_2$ as a crystalline powder.

290. Potassium chromate and dichromate do not precipitate strontium solutions. In strong and neutral solutions the chromate may give a precipitate, but not in presence of acetic acid.

291 Commercial Strontium Compounds:

The only compound of importance is the nitrate, which is used for red fire.

CALCIUM.**Blowpipe Test.**

292. In the flame calcium compounds give a reddish-yellow color. If the color is seen through a blue glass it appears greenish-gray.

Solution Tests.

293. Hydrochloric acid does not affect calcium solutions.

294. Nitric acid behaves like hydrochloric acid.

295. Ammonium hydroxide does not precipitate calcium solutions if the hydroxide be free from carbonate,

296. Sodium and potassium hydroxides behave very much the same as with barium solutions.

297. Alkaline carbonates (of K, Na and NH_4) give a white precipitate of calcium carbonate CaCO_3 , which is soluble in dilute acids. If the alkaline carbonate be added to an acid solution, the precipitation is only complete after boiling. The precipitate is slightly soluble in ammonium chloride.

298. Sulphuric acid and soluble sulphates do not precipitate calcium in dilute solutions. In strong solutions, sulphuric acid may give calcium sulphate CaSO_4 , which is soluble in much water and in acids. Alcohol assists the precipitation of calcium sulphate. The precipitate is readily soluble in ammonium sulphate on boiling.

299. Calcium sulphate does not precipitate calcium solutions.

300. Hydrofluosilicic acid does not affect calcium solutions, even in the presence of alcohol.

301. Sodium phosphate gives white calcium phosphate CaHPO_4 , which is soluble in dilute acids. It is slightly soluble in ammonium chloride.

302. Ammonium oxalate gives calcium oxalate CaC_2O_4 as a fine white powder. It is readily soluble in hydrochloric or nitric acid, but not in oxalic or acetic acid.

303. Potassium chromate and dichromate do not affect calcium solutions.

304. Commercial Calcium Compounds :

Lime is calcium oxide ; it is sometimes called quicklime.

Slaked lime is calcium hydroxide.

Air-slaked lime is a mixture of calcium hydroxide and carbonate.

Chalk is calcium carbonate.

Plaster of Paris is calcium sulphate.

Land plaster is calcium sulphate with water of crystallization.

Bone ash is calcium phosphate.

Bone black is a mixture of calcium phosphate and carbon.

Chloride of lime is calcium hypochlorite and chloride.

Bleaching powder is the same as the preceding.

CHAPTER X.

SEPARATION OF THE METALS OF THE FIFTH GROUP.

305. This group of metals is contained in the filtrate obtained from the precipitate of the fourth group of metals. It contains all the reagents that have been used to precipitate the metals of the preceding groups. It will be remembered that we have added to it hydrochloric acid, hydrogen sulphide, ammonium chloride, ammonium hydroxide, ammonium sulphide and ammonium carbonate. From the fact that we have added the ammonium hydroxide to more than neutralize the hydrochloric acid first added, the fluid is now alkaline.

306. If the original material contained ammonium compounds, these could not now be detected in this filtrate, because we have also added these as we have proceeded with the analysis. We must therefore test for ammonium compounds by taking some of the original material, and before we have added anything to it. This original material is mixed with sodium hydroxide in excess, in a test-tube; the top of the tube is closed with the thumb, and the contents gently warmed. By placing the tube under the nose and removing the finger, the odor of ammonia gas will be noted and indicates the presence of ammonium compounds.

307. The filtrate containing the metals of the fifth group is divided into two parts, one a small quantity and the other the balance of the fluid.

308. To the smaller portion disodium orthophosphate is added. If this gives a fine crystalline precipitate, it is magnesium ammonium phosphate, and indicates the presence of magnesium of the fifth group of metals. Sometimes a light, flocculent precipitate is obtained at this point. This may be aluminium phosphate; but if it is allowed to settle, then shaken up with a little water, allowed to settle again and the water poured off, it will be

found to be soluble in sodium hydroxide if it is aluminium phosphate. Magnesium-ammonium phosphate is insoluble in sodium hydroxide but becomes magnesium hydroxide, and flocculent.

309. The larger portion of the fluid (**307**) is evaporated to dryness, care being taken to avoid loss by spattering. The dish is very gradually heated over the flame, and kept at a good heat until no more white fumes are seen, when the flame is removed for a moment. This causes the ammonium compounds to be decomposed and driven off.

310. Having expelled all volatile matter, allow the dish to cool, and then dissolve the residue in a little water. Filter the fluid through a very small filter into a clean test-tube. Test some of the filtrate on a clean platinum wire in the Bunsen flame. A yellow flame indicates the presence of sodium. A lilac-colored flame indicates the presence of potassium.

311. If sodium is found by the flame test, there is no evidence that potassium is absent or present, because the yellow color of the sodium flame is so intense that it covers the potassium color, which is masked by the former. In this case, the flame may be observed through a blue glass, when the lilac-color can be seen and the yellow is cut off. In order to prove the presence of potassium, we put two or three drops of the fluid **310** into a watch-glass, and add to it two or three times its volume of platinic chloride, stirring the mixture with a glass rod. A fine yellow precipitate of potassium-platinum chloride (octohedra under a lens) indicates the presence of potassium in the fluid.

312. If much magnesium is present, and the solution containing the sodium and potassium, after heating, is concentrated, it is best to add enough milk of lime to it to make it alkaline to red litmus paper; then warm it, and filter. This precipitates the magnesium as hydroxide. To the filtrate from the milk of lime ammonium carbonate is added; it is gently warmed, and then filtered. This filtrate is evaporated to dryness and heated to expel ammonium salts, as explained above. The residue may now be dissolved in water and tested for sodium and potassium, as in **311**. This whole procedure may be omitted in a large majority of cases; for if only a moderate quantity of magnesium is present with the sodium and

potassium, it will be made insoluble by heating (309), and little of it will pass into solution when the ignited residue is treated with water. A strong solution of magnesium chloride will give a precipitate with platinum chloride that resembles the potassium-platinum salt.

The reasons for the method of procedure with the fluid containing the metals of the fifth group are as follows :

313. The alkaline filtrate is in the proper condition for the precipitation of magnesium with disodium orthophosphate ; we therefore take a small portion of it to make the test. The precipitate is a very characteristic one, and will readily be recognized after first acquaintance.

314. As the filtrate contains a large quantity of ammonium salts which we have added in the course of the separation of the metals of the first four groups, and as these ammonium salts interfere with one of the tests for potassium, we have to remove them before we can proceed. As all ammonium salts are volatile when heated, the evaporation of the balance of the filtrate not used for the magnesium test, and the heating of the dry residue, give us a method of removing them without interfering with the sodium and potassium compounds present, which are not volatile when heated.

315. The testing of the water solution of the residue in the flame tells us if either sodium or potassium is present. But if sodium is present, potassium may also be with it and its color in the flame be masked by the bright yellow of the former metal. A piece of blue glass will often cut off the yellow flame of sodium and reveal the lilac color of potassium, but the test with platinum chloride should always be applied to make sure of the presence of potassium.

316. Platinum chloride gives, with ammonium salts, a fine yellow precipitate of ammonium-platinum chloride, which it is practically impossible to distinguish from the potassium compound by its appearance. It is therefore exceedingly important that all ammonium salts should be expelled by heat before making the test with platinum chloride as explained above. The white fumes obtained, when heating the residue from the evaporation of

the fluid containing the fifth group is a guide as to the expulsion of ammonium salts; when the fumes cease, all these salts have volatilized.

317. The test for ammonium compounds made on the original material with sodium hydroxide depends on the fact that all ammonium salts are decomposed, and ammonia gas is evolved when they are heated with alkaline hydroxides. If the nose is not sensitive to small quantities of ammonia, moistened red litmus paper should be held over the mouth of the test-tube so that the vapors pass it; it will be turned blue if ammonia gas is evolved.

The above course of procedure is tabulated in the following scheme:

TABLE V. Alkali Group.

Divide Solution in two parts.

Part I, Small. — Add Na_2HPO_4 . A fine crystalline ppt. is MgNH_4PO_4 and indicates **Mg**.

Part II, Large. — Evaporate to dryness, heat till all white fumes cease. Cool, dissolve in water, filter out insoluble and reject it. Test solution on Pt wire in Bunsen flame. Yellow flame indicates **Na**. Observe flame through blue glass, lilac flame indicates **K**. Confirm presence of **K** by adding PtCl_4 and alcohol to a few drops of solution in a W.G. Yellow ppt. on stirring indicates **K**.

N. B. — NH_4 salts must be looked for in the original solution before adding any reagents whatever. To test for NH_4 salts add to the original solution an excess of NaOH and observe the odor of the gas evolved on warming. Pungent NH_3 odor indicates **NH_4 Salts**.

CHAPTER XI.

SPECIAL TESTS FOR THE METALS OF THE FIFTH GROUP.

MAGNESIUM.

The blowpipe test for magnesium is of little value.

Solution Tests.

Hydrochloric acid does not affect magnesium solutions.

Nitric acid does not affect magnesium solutions.

Hydrogen sulphide does not affect magnesium solutions.

318. Ammonium hydroxide precipitates part of the magnesium from its solutions as hydroxide, $\text{Mg}(\text{OH})_2$. The precipitate is soluble in ammonium chloride, and this latter fact constitutes the reason for the addition of the ammonium chloride in the course of systematic analysis.

319. Alkaline hydroxides (of K, Na, Ca and Ba) give a precipitate of magnesium hydroxide, $\text{Mg}(\text{OH})_2$. Boiling promotes the precipitation. Ammonium chloride dissolves these precipitates if they are separated from the fluid and washed.

320. Ammonium carbonate does not precipitate magnesium solutions unless they are allowed to stand for some time. Strong solutions may be precipitated. The precipitation is prevented by ammonium chloride, except in strong solutions.

321. Alkaline carbonates (of K and Na) give a precipitate of basic magnesium carbonate, 4MgCO_3 , $\text{Mg}(\text{OH})_2$, but some of the magnesium remains in solution until the fluid is boiled, when a further precipitation takes place. Ammonium chloride in quantity prevents this precipitation, and also dissolves the precipitate if it is separated and washed.

322. Disodium orthophosphate gives a precipitate of hydro-magnesium phosphate MgHPO_4 as a white powder. This is formed in absence of ammonium salts.

323. Ammonium chloride and ammonium hydroxide, added to a magnesium solution and followed by disodium orthophosphate, give a precipitate of magnesium-ammonium phosphate, MgNH_4PO_4 , which is crystalline and very characteristic. In very dilute solutions it separates slowly, and stirring promotes its formation. Water and ammonium salts dissolve the precipitate very slightly. Water with ammonium hydroxide does not dissolve it, but acids, even acetic acid, dissolve it.

324. Ammonium oxalate does not precipitate dilute solutions of magnesium, but in strong solutions ammonium-magnesium oxalate is formed. Ammonium chloride with ammonium hydroxide interferes with this precipitation, but does not prevent it.

Sulphuric acid does not affect magnesium solutions.

Hydrofluosilicic acid also does not affect these solutions.

Potassium chromate produces no precipitate.

325. Commercial Magnesium Compounds:

Epsom salt is magnesium sulphate.

Magnesia is magnesium oxide.

Magnesia alba is also magnesium oxide.

Magnesia ponderosa is magnesium oxide of a denser and more compact kind.

Light carbonate of magnesia is a mixture of magnesium carbonate and hydroxide. This is sometimes called magnesia levis.

Heavy carbonate of magnesia is also a mixture of carbonate and hydroxide. This is sometimes called magnesia ponderosa.

Dolomite is a variety of marble containing magnesium carbonate.

Asbestos is a magnesium silicate.

Talcum, meerschaum and serpentine are also silicates of this metal.

The "triple phosphate" found in urine is ammonium-magnesium phosphate.

POTASSIUM.

Blowpipe Test.

326. In the flame potassium gives a lilac-colored tint.

Solution Tests.

327. Platinum chloride produces in acid or neutral solutions of potassium a fine heavy precipitate of potassium platonic chloride,

K_2PtCl_6 . It consists of microscopic octohedra which are almost insoluble in water, quite so in alcohol, and the solubility of which is not promoted by acids. The test is best made in a watch-glass, and stirring promotes the precipitation. Alkaline solutions are made acid by carefully adding hydrochloric acid before adding the platinum chloride.

328. Sodium acid tartrate gives potassium acid tartrate, $KHC_4H_4O_6$, as a white crystalline precipitate. Stirring promotes the precipitation, which is best made in a watch glass. Alkaline hydroxides dissolve the precipitate; it is also soluble in acids. Therefore acid solutions should be nearly neutralized with sodium carbonate before this test is applied.

329. Tartaric acid produces potassium acid tartrate the same as with sodium acid tartrate.

330. Commercial Potassium Compounds:

Caustic potash is potassium hydroxide. Is sometimes called "potash."

Potashes are impure potassium carbonate and hydroxide from wood ashes.

Pearl ash is purified wood ashes, and is a potassium carbonate.

Salt of tartar is potassium carbonate made from argols.

Saltpetre is potassium nitrate. Is sometimes called "nitre."

Cream of tartar is acid tartrate of potassium.

Soft soap is potassium soap.

Rochelle Salt is double tartrate of potassium and sodium.

Hepar sulphuris or liver of sulphur is a mixture of potassium sulphides.

SODIUM.

Blowpipe Test.

331. In the flame, sodium compounds give an intense yellow color. A piece of cobalt blue glass entirely cuts off this color of the flame. This is the most important test for sodium compounds.

Solution Tests.

332. Sodium solutions do not give any precipitates with platinum chloride, tartaric acid or acid tartrate of sodium.

333. Commercial Sodium Compounds:

Common or table salt is sodium chloride.

Soda used for washing is sodium carbonate with crystal water. Is sometimes called "soda crystals."

Sal soda is another name for washing soda or sodium carbonate crystals.

Caustic soda is sodium hydroxide.

Soda ash is crude sodium carbonate.

Glauber's salt is sodium sulphate with crystal water.

Chili saltpetre is sodium nitrate.

Sodium hyposulphite is sodium thiosulphate.

Phosphate of soda is disodium hydrogen phosphate.

Borax is sodium pyroborate.

Water glass is sodium silicate in strong solution.

Salt cake or nitre cake is sodium sulphate.

AMMONIUM.

Blowpipe Test.

334. All ammonium compounds are volatile when heated in the flame.

Solution Tests.

335. Alkaline hydroxides (of K, Na, Ca or Ba), when mixed with ammonium compounds, either solid or liquid, and warmed, cause the evolution of ammonia gas, which is recognized by its odor or its action on test papers.

336. Platinum chloride gives a fine yellow precipitate of ammonium platonic chloride $(\text{NH}_4)_2\text{PtCl}_6$. It consists of microscopic octohedra. The precipitate is exceedingly like the potassium compound in appearance.

337. Sodium acid tartrate gives a precipitate of ammonium acid tartrate $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$. Stirring and shaking promote the precipitation.

338. Tartaric acid gives the same precipitate as sodium acid tartrate, but only in strong solutions.

339. Nessler's solution added to a solution of ammonium salts gives a reddish-brown precipitate $\text{Hg}_2\text{NH}_2\text{OI}$. In very dilute solu-

tions only a yellowish brown coloration is produced. The test is extremely delicate and is used in water analysis. For Nessler's solution see 5c.

340. Commercial Ammonium Compounds :

Gas liquor is a water solution of ammonium carbonate, sulphate and sulphide from the gas-works using soft coal. A similar fluid is obtained in making boneblack.

Sal ammoniac is ammonium chloride.

Ammonia or spirits of hartshorn is a solution of ammonium hydroxide.

Carbonate of ammonia is a mixture of carbonate and carbamate. This is sometimes called "sal volatile."

Ammonia used in fertilizers is present as sulphate.

CHAPTER XII.

SEPARATION AND DETECTION OF THE ACID RADICALS OR ACIDS.

341. The words "acid radicals" are intended to convey to the mind the idea of that part of the formula of a salt remaining after the metal has been taken away. It must not be supposed that the combinations thus left have any existence; they only represent the salt formula from which the metal was removed. Thus, if we take the metal away from the formula of any sulphate, we have SO_4 left, and this is the so-called radical of sulphuric acid. Again, if we take the metal away from the formula of any nitrate, we have NO_3 left, and this is the radical of nitric acid. Or, in the case of any chloride, if we take away the metal we have left only Cl , which is the radical of hydrochloric acid. In the case of any bromide we have Br left, and so on. Therefore we shall study the properties of the various acid radicals in the succeeding pages of this volume, looking upon them as the representatives of the salts of the metals.

As in the case of the metals, we shall treat only of those acid radicals which are common, and which serve as illustrations of the methods of procedure.

342. The substance or solution is assumed to contain one or more of the following acid-radicals:

S	of	sulphides.	AsO_4	of	arsenates.
Cl	"	chlorides.	SO_4	"	sulphates.
Br	"	bromides.	SO_3	"	sulphites.
I	"	iodides.	SiO_3	"	silicates.
F	"	fluorides.	CN	"	cyanides.
NO_3	"	nitrates.	$\text{Fe}(\text{CN})_6$	"	ferrocyanides.
ClO_3	"	chlorates.	$\text{Fe}(\text{CN})_6$	"	ferricyanides.
BO_3	"	borates.	C_2O_4	"	oxalates.
CO_3	"	carbonates.	$\text{C}_4\text{H}_4\text{O}_6$	"	tartrates.
CrO_4	"	chromates.	$\text{C}_6\text{H}_5\text{O}_7$	"	citrates.
PO_4	"	phosphates.	$\text{C}_2\text{H}_3\text{O}_2$	"	acetates.
AsO_2	"	arsenites.			

The method of procedure for their detection is as follows :

343. *If the material is a fluid*, evaporate half of it very carefully to dryness, avoiding overheating. The solid residue is submitted to the following tests, using a small and *fresh portion* for each experiment. *If the material is a solid* it may be used at once.

344. A.—Heat on charcoal before the blowpipe.

The substance *deflagrates* : indication of the presence of nitrates or chlorates or both.

The substance *carbonizes* : indication of an organic acid.

345. B.—If the substance deflagrates on charcoal, put a little of it upon the surface of a few drops of sulphuric acid in a watch-glass. A yellowish-brown color and a chlorous odor indicate *chlorates*.

346. C.—If the substance deflagrates on charcoal, put a little of it into a test-tube, add sulphuric acid, and then pour upon the top of the mixture a strong solution of ferrous sulphate. A dark brown ring at the junction of the two fluids indicates *nitrates*.

347. In the two last tests the color due to the presence of chlorates or nitrates may be completely masked by a deep brown color from iodides, or an orange-red color from bromides, if either of them are present. To test for nitrates or chlorates in presence of iodides or bromides, the following methods are used :

348. For *nitrates*. If ammonium salts have been found while testing for the metals, boil some of the original material (solution or solid) with excess of sodium carbonate until it is almost reduced to dryness, to expel ammonia. To this fluid now add a little water, a few drops of sulphuric acid until it is acid to test paper, a drop or two of copper sulphate and then a piece of sheet zinc. Allow the action to go on for five minutes ; and if there is not a brisk action, add a few more drops of acid. This will convert the nitrates into ammonium compounds, and if sodium hydroxide in excess is added to some of the mixture poured into another tube, the odor of ammonia gas will be noted on warming. This is an indication the presence of nitrates.

349. For *chlorates*. To a solution of the original material add nitric acid in excess and then silver nitrate until it will produce no more precipitate. This will precipitate all chlorides, bromides, iodides, cyanides, ferrocyanides, ferricyanides and sulphides. Filter out the precipitate and reject it. To the filtrate add sodium carbonate in slight excess, boil and filter. This will precipitate any silver that may be present, and the filtrate will contain the chlorates if they are present. Add excess of sulphuric acid to the filtrate, then a drop or two of copper sulphate and a piece of sheet zinc. Allow the action to go on for five minutes, and if it is not brisk, add a few more drops of sulphuric acid. Pour off the fluid from the zinc, add to it a few drops of nitric acid and then silver nitrate. A white precipitate, soluble in excess of ammonium hydroxide, indicates the presence of chlorates. The chlorates do not give a precipitate with silver nitrate, but the zinc and sulphuric acid reduce them to chlorides, which give a precipitate.

350. D.—Put a little of the substance into a test-tube and pour upon it dilute hydrochloric acid (1 in 3). If a gas is given off, note its odor.

If it has the odor of hydrogen sulphide, *sulphides* are present.

351. If it has the odor of burning sulphur, it indicates the presence of *sulphites*.

352. If it has the odor of hydrocyanic acid, *cyanides* are present.

353. If it has no odor, it is probably carbon dioxide. In this case take some clear lime water and pour the *gas* from the test-tube into it, shaking the lime water. The formation of a white precipitate indicates the presence of *carbonates*.

N. B. Always apply the lime water test, even when an odor of other acids is obtained.

354. There are several precautions necessary in applying the tests under D. In the first place, the dilute hydrochloric acid must be free from odor before it is put upon the substance to be tested. To secure this freedom from odor, the strong acid is mixed with the water in a test tube, and the mixture is well shaken, until, on applying the nose, no odor is detected in the tube.

This is especially necessary in the detection of sulphites and cyanides. The second precaution to be taken is, in testing for carbon dioxide, that none of the acid fluid falls into the lime water when the gas is poured into the tube.

355. E.—Mix some of the substance to a paste with sulphuric acid in a watch-glass, and test a portion of the mixture in a blowpipe flame on a platinum wire which has been moistened with strong glycerin. A flame having a leaf-green border indicates *borates*. The test is very delicate, but the duration of the color is very short. In presence of copper and barium, apply this test to some of the solution, see **370**.

356. F.—Put some of the substance into a test-tube and add a few drops of alcohol to it, then pour into the mixture a few drops of sulphuric acid, warm it, and note the odor. An odor of acetic ether indicates *acetates*. If acetates are present, a carbonizing of the substance will have been noted in **344**.

357. G.—Mix the substance with sulphuric acid in a watch-glass and set it aside for ten minutes. Wash out the mixture with water and note if the surface of the glass has been roughened where the mixture was in contact with it. The effect is best seen by drying the glass and then breathing upon it. Such roughening indicates the presence of *fluorides*.

Care should be taken that the glass is not rough before testing in it.

358. H.—Mix the substance with enough nitric acid to turn blue litmus paper red and then dry the mixture. To the residue add nitric acid again, warm it gently and add water to this mixture; if there is any matter that remains insoluble in water after stirring, it is silica, and indicates the presence of *silicates*. Test the insoluble matter in the sodium metaphosphate bead, see **482**.

359. Add to the *solution* of the substance (or boil the *solid* with) a solution of sodium carbonate (1 in 5) until it is decidedly alkaline to red litmus paper. Boil for some minutes and filter

the fluid while it is hot. Test the precipitate, or insoluble, if any for silicates, fluorides and phosphates. Use the solution for the following tests, taking a *separate* quantity for each.

360. a.—To the solution add nitric acid until it is acid to test paper. Then add silver nitrate. A white curdy precipitate indicates the presence of either chlorides, bromides, iodides, cyanides, ferrocyanides, ferricyanides or sulphides, or all of them. No precipitate with silver nitrate indicates the absence of these radicals.

Having added an excess of silver nitrate to the acid solution, to be sure that no more precipitate is obtainable, shake the mixture well and allow the precipitate to settle. Pour off the fluid and reject it. Shake the precipitate with a little water, allow it to settle and again pour off the fluid and reject it. To the washed precipitate add ammonium hydroxide, shake well and filter.

The insoluble matter may contain silver iodide, bromide, ferrocyanide, or sulphide, or all of these.

The solution may contain silver chloride, cyanide or ferricyanide, or all of these. Now add nitric acid to the solution until it reddens blue litmus paper, when a precipitate of the three last silver compounds will be obtained, or of any one of them, if they are present. If a precipitate is not obtained, they are not present.

If the precipitate is entirely soluble in ammonium hydroxide, one or all of the last three silver compounds may be present.

In case a portion of the silver precipitate is soluble and another portion insoluble in ammonium hydroxide, all of them may be present, and all the tests given below must be made.

361. b.—Add hydrochloric acid until just acid to litmus paper. In a separate test-tube, generate a little chlorine gas, with hydrochloric acid and potassium chlorate. Pour *a little* of this gas into the acid fluid previously prepared, and shake the mixture. A dark brown fluid, a few drops of which gives a deep blue color with cold starch paste indicates the presence of *iodides*.

Bismuth
HCl sol white ppt. On CCl₄ solub
in strong acids

H₂S in black ppt.

Alk. hydros white ppt. of Bi(OH)₃

Copper

HCl sol green color

H₂S in black solution

Alk. hydros - light blue ppt.

H₂SO₄ (H₂O) red in ppt.

Cadmium

H₂S gives bright yellow ppt. - CdS

Alk. hydros white ppt.

" Carbon - " "

Chromium

HCl no effect

362. *c.*—If iodides have been found in *b*, add carbon disulphide, and then hydrochloric acid in excess. To this fluid add sodium hypochlorite, drop by drop, shaking the mixture, and keeping it acid. In presence of iodides, the carbon disulphide is first colored violet by separated iodine, and, as the hypochlorite is added, this color is bleached out, or it gives place to a yellow-brown color of separated bromine, which indicates *bromides*. Extreme care is necessary to avoid adding too much hypochlorite, but the test is a very good one.

363. *d.*—If the precipitate in *a* is partly or entirely soluble in ammonium hydroxide, chlorides and cyanides may be present. To determine if chlorides are present (cyanides are found in **350**), wash and dry some of the precipitate soluble in ammonium hydroxide (reprecipitating it with nitric acid, see **360**), and melt it in a small porcelain dish. Silver cyanide is decomposed, while the chloride is not affected. After cooling, add a little water to the dish, and place in contact with the melted precipitate a piece of zinc, adding sulphuric acid until a brisk action takes place. This converts the silver chloride into silver, and zinc chloride is formed in solution. After a few minutes, filter, add nitric acid to the filtrate, and then silver nitrate. A white precipitate, soluble in ammonium hydroxide, indicates *chlorides*.

364. *e.*—Add excess of hydrochloric acid and then ferrous sulphate; a blue precipitate indicates the presence of *ferricyanides*.

365. *f.*—Add excess of hydrochloric acid and then ferric chloride; a blue precipitate indicates *ferrocyanides*.

N. B.—No test is required here to determine the presence of cyanides; these should have been found already in **352**.

366. *g.*—Add hydrochloric acid in excess and boil (solution should be acid after boiling), and then barium chloride; a white precipitate indicates the presence of *sulphates*.

367. *h.*—If the solution **359** is yellow, add excess of acetic acid and then lead acetate; a yellow precipitate, soluble in sodium hydroxide, indicates *chromates*.

If the solution is not yellow, chromates are absent.

368. i.—Add nitric acid in excess and boil the mixture. Add a few drops of this mixture to molybdic solution and warm; a yellow precipitate indicates *phosphates*.

369. N. B.—If arsenic has been found when testing for the metals, a test must be made to determine if arsenic acid is present. In this case add excess of nitric acid to the solution **359** and then silver nitrate until it gives no more precipitate. Filter out this precipitate, if any, and reject it. To the filtrate add ammonium hydroxide in such a manner that it floats upon the surface of the fluid. A reddish-brown precipitate at the junction of the two fluids indicates *arsenates*. A yellow precipitate here indicates *arsenites*. If arsenates are found, the yellow precipitate (**368**) may contain this acid radical. In this case add to solution **359** an excess of hydrochloric acid, then heat to near the boiling point and pass hydrogen sulphide. Continue passing the gas and warming the solution for five minutes; this will precipitate the arsenic of both arsenates and arsenites. Filter out the precipitate, add nitric acid, and boil, to decompose hydrogen sulphide. Filter if necessary, add a few drops of the filtrate to molybdic solution and warm the mixture; a fine yellow precipitate now indicates the presence of *phosphates*.

370. j.—If copper or barium is present, the solution **359** must be tested for borates. For this purpose evaporate some of it nearly to dryness, add sulphuric acid to form a paste and then test with glycerin in the blowpipe flame; a leaf-green border to the flame indicates *borates*. See **355**.

371. k.—Add hydrochloric acid in excess, and boil (the fluid should be acid after boiling), then add dilute sodium hydroxide (1 of solution and 4 of water) drop by drop until the fluid is just alkaline. To this add calcium chloride; a white precipitate indicates oxalates or tartrates, or both.

Filter out the precipitate and test the filtrate with more calcium chloride to see if precipitation is complete. The filtrate freed from oxalates or tartrates is rejected.

The precipitate is washed with acetic acid on the filter and the solution passing through is allowed to run into a test-tube. If the substance contains potassium, a crystalline precipitate of acid tartrate of potassium may separate

in the acetic acid filtrate; this is allowed to remain. The acid is passed through the filter several times to see if all the precipitate will dissolve. If it all dissolves, only tartrates are present, and on adding dilute sodium hydroxide (see above) to the acetic acid fluid until it is just neutral, calcium tartrate is precipitated again. This latter should be filtered out, partially dried on the filter paper and then heated on platinum foil. An odor of burning grapes indicates *tartrates*. If tartrates are present, the substance carbonizes on charcoal (see **344**). The precipitate, insoluble in acetic acid, should be dissolved in hydrochloric acid, the solution mixed with an excess of ammonium hydroxide, which again gives a precipitate of calcium oxalate insoluble in acetic acid, indicating the presence of *oxalates*.

- 372.** 1.—Add hydrochloric acid until the fluid is just acid to litmus paper. Now boil the mixture for some time and test again with litmus paper. If the paper turns red, add dilute sodium hydroxide (1 of solution, 4 of water), drop by drop, until the fluid is neutral, that is, does not change the color of the test paper. Add some of this solution to a test-tube full of lime water. If a precipitate is formed, filter it out (it is probably calcium oxalate or tartrate), and boil the filtrate; a precipitate indicates *citrates*. If citrates are present the substance will carbonize on charcoal (see **344**).

CHAPTER XIII.

SPECIAL TESTS FOR THE ACID RADICALS OR ACIDS.

NITRATES.

Blowpipe Test.

373. Nitrates deflagrate when heated on charcoal, before the blowpipe flame. The red-hot coal must be in contact with the nitrate.

Solution Tests.

374. All nitrates which are not basic salts are soluble in water.

375. Hydrogen nitrate HNO_3 , (strong nitric acid) produces an intense yellow color when placed in contact with nitrogenous organic bodies, as white feathers, wool, skin, etc. Heat promotes the action.

376. Copper, in contact with a nitrate and sulphuric acid, gives fumes which, when mixed with air, form red nitrogen tetroxide.

377. Ferrous sulphate, in strong solution, poured onto a mixture of a nitrate with a large excess of sulphuric acid, gives a dark brown ring at the junction of the two fluids. With traces of nitrate, this color is purplish-brown. Iodides, bromides, chlorates and chromates interfere with this test.

378. Zinc amalgam reduces nitrates to nitrites and, if sulphuric acid, potassium iodide and starch paste are added to the fluid, a blue color will be obtained. The nitrous acid, set free by the sulphuric acid, liberates iodine, and this gives the blue color with the starch.

379. Zinc-copper couple (formed by adding a few drops of copper sulphate to a solution containing a piece of sheet zinc) and sulphuric acid converts nitrates into ammonium compounds. After this action has continued for some minutes, the solution will give the odor of ammonia gas on adding sodium hydroxide

in excess and warming. This test serves to detect nitrates in presence of chlorates, iodides, bromides and chromates.

CHLORATES.

Blowpipe Test.

380. Chlorates deflagrate when heated on charcoal, before the blowpipe flame. The red-hot coal must be in contact with the chlorate.

381. Heat converts alkaline chlorates into chlorides, which on dissolving give the tests for this latter radical. The heating is best done on a piece of porcelain.

Solution Tests.

382. All chlorates are soluble in water.

383. Hydrogen chlorate HClO_3 (chloric acid) is rarely seen, but in color and odor it resembles nitric acid.

384. Sulphuric acid in a watch-glass is colored yellow if a little chlorate is dropped into it, and an extremely characteristic odor is evolved. A little experience is necessary in the recognition of this odor, but, when once fairly known, it is the most convenient test for chlorates. In making the test, great care must be taken not to heat the mixture, as the compound formed is explosive at a moderate temperature.

385. Zinc-copper couple (formed as in **379**) and sulphuric acid reduces chlorates to chlorides. If the action is continued for some minutes and then nitric acid and silver nitrate are added, a white precipitate, soluble in excess of ammonium hydroxide, is obtained. Compare **387**. Chlorates do not give a precipitate with nitric acid and silver nitrate. In presence of chlorides, bromides, iodides, etc., silver nitrate must first be added until it will not give any more precipitate, and this precipitate filtered out. To the filtrate the above mentioned test with zinc-copper couple may be applied.

CHLORIDES.

The blowpipe tests for chlorides are of no value.

Solution Tests.

386. Hydrogen chloride HCl is a gas very soluble in water, yielding a liquid known as hydrochloric acid.

387. Silver nitrate in presence of nitric acid gives a precipitate of silver chloride AgCl , which is soluble in ammonium hydroxide and potassium cyanide. It is insoluble in dilute nitric acid, melts without decomposing when gently heated, and is blackened on exposure to daylight.

388. Lead acetate gives a precipitate of lead chloride PbCl_2 . It is soluble in a large amount of water, and readily so in boiling water. It is less soluble in dilute nitric and hydrochloric acids than in water. It is soluble in acetic acid and alkaline acetates.

389. Mercurous nitrate gives a precipitate of mercurous chloride, Hg_2Cl_2 (calomel). It is insoluble in dilute nitric and hydrochloric acids. Aqua regia dissolves it. Alkaline hydroxides decompose it.

390. Manganese dioxide and sulphuric acid in presence of a chloride give chlorine gas on heating. The gas may be detected with moist litmus paper or indigo solution on filter paper, both of which are bleached.

391. Sulphuric acid heated with a dry chloride gives hydrogen chloride as a gas, which may be detected by its odor, and the white fumes it gives with ammonium hydroxide held over it on a glass rod. Insoluble chlorides are not decomposed.

BROMIDES.

The blowpipe tests for bromides are of little value.

Solution Tests.

392. Hydrogen bromide HBr is a gas very soluble in water, giving a fluid that resembles hydrochloric acid. The solution is called hydrobromic acid, and turns yellow on keeping, owing to the separation of bromine.

393. Silver nitrate in presence of nitric acid gives a yellowish-white precipitate of silver bromide AgBr . It is insoluble in dilute nitric acid, but slightly soluble in ammonium hydroxide. It is readily soluble in potassium cyanide. It turns gray on exposure to daylight.

394. Chlorine (either as gas or in solution) separates bromine from bromides (but not from insoluble bromides), and the separated

bromine colors the fluid yellow. Care must be taken to avoid excess of chlorine, as this bleaches out the color, owing to the formation of bromine chloride.

395. Carbon disulphide (or chloroform) added to a solution containing separated bromine dissolves it out of the fluid on shaking, and the carbon disulphide (or chloroform) becomes yellowish-brown.

396. Manganese dioxide and sulphuric acid, in presence of a bromide produce red vapors of bromine on heating. The red vapors will color starch paper yellow.

397. Sulphuric acid heated with a dry bromide produces reddish-brown vapors of bromine. Insoluble bromides are not decomposed.

IODIDES.

The blowpipe tests for iodides are of little value.

Solution Tests.

398. Hydrogen iodide, HI (hydriodic acid), is a gas very soluble in water, yielding a fluid resembling hydrochloric acid. The solution turns reddish-brown on keeping, owing to the separation of iodine.

399. Silver nitrate, in presence of nitric acid, produces a yellowish-white precipitate of silver iodide AgI . It is insoluble in dilute nitric acid, very slightly soluble in ammonium hydroxide, but dissolves in potassium cyanide. It turns black on exposure to daylight.

400. Copper sulphate 1 part, with ferrous sulphate $2\frac{1}{2}$ parts, gives in neutral solutions a precipitate of cuprous iodide Cu_2I_2 , which is dirty white. A little ammonium hydroxide assists the precipitation. Chlorides and bromides do not affect this result.

401. Chlorine (either as gas or in solution) separates iodine from iodides (but not from insoluble iodides); and the separated iodine may appear as a brown precipitate, or it will give a red-brown fluid according to the quantity separated. Excess of chlorine bleaches the fluid owing to the formation of iodine chloride, therefore care must be used not to add too much of the gas.

402. Starch paste (made by adding to boiling water a little cream of starch made with cold water, and cooling) gives an in-

tense blue color with separated iodine. Heat destroys the color, hence the fluid tested must be cold.

403. Carbon disulphide (or chloroform) added to a fluid containing separated iodine dissolves it out on shaking and becomes violet.

404. Manganese dioxide and sulphuric acid in presence of an iodide, give violet vapors of iodine on heating. These vapors color starch paper deep blue. Insoluble iodides are not decomposed.

405. Sulphuric acid, heated with a dry iodide, gives violet vapors of iodine. Insoluble iodides are not decomposed.

CYANIDES.

The blowpipe tests for cyanides are of little value.

Solution Tests.

406. Hydrogen cyanide HCN (hydrocyanic or prussic acid) is a very volatile, inflammable liquid, which is soluble in water and extremely poisonous. It has a very characteristic odor, somewhat like bitter almonds, and its solution in water does not redden blue litmus paper.

407. Silver nitrate, in presence of nitric acid, gives a precipitate of silver cyanide AgCN. It is insoluble in dilute nitric acid, but dissolves in ammonium hydroxide and potassium cyanide. This precipitate is decomposed by gentle ignition, producing metallic silver, which dissolves in dilute nitric acid.

408. Ferrous sulphate with a few drops of ferric chloride, added to a solution of a cyanide made acid with hydrochloric acid, and followed by sodium hydroxide in excess, if the mixture is heated for five minutes, will produce a bluish-green precipitate. This is a mixture of ferric ferrocyanide (Prussian blue) and ferrosiferrous hydroxide. On adding hydrochloric acid to this mixture, the hydroxide is dissolved, leaving the blue ferric ferrocyanide. In dilute solutions of cyanides the fluid is green after adding the acid, but a blue precipitate settles on standing.

409. Ammonium sulphide (yellow with sulphur) added to a cyanide until the fluid is yellow, followed by ammonium hydroxide,

gives ammonium sulphocyanide when the mixture is warmed in a dish to expel the excess of ammonium sulphide. If this fluid is now made acid with hydrochloric acid and ferric chloride added, a blood-red color is obtained ; see **201**.

FERROCYANIDES.

410. All ferrocyanides are decomposed when heated to redness.

Solution Tests.

411. Ferric chloride gives a blue precipitate of ferric ferrocyanide (Prussian blue), $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, insoluble in hydrochloric acid, and decomposed by alkaline hydroxides with separation of ferric hydroxide.

412. Copper sulphate gives a precipitate of copper ferrocyanide $\text{Cu}_2\text{Fe}(\text{CN})_6$, having a reddish-brown color. It is insoluble in dilute acids, and decomposed by alkaline hydroxides.

413. Silver nitrate gives a precipitate of white silver ferrocyanide $\text{Ag}_4\text{Fe}(\text{CN})_6$ which slowly turns blue. It is insoluble in dilute nitric acid and also in ammonium hydroxide. It is soluble in potassium cyanide, and is decomposed when boiled with ammonium hydroxide.

FERRICYANIDES.

414. All ferricyanides are decomposed when heated to redness.

Solution Tests.

415. Ferric chloride does not precipitate these solutions.

416. Ferrous sulphate gives a blue precipitate of ferrous ferricyanide $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$. It is insoluble in hydrochloric acid, and decomposed by alkaline hydroxides.

417. Copper sulphate gives a yellowish-green precipitate of copper ferricyanide $\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$. It is insoluble in hydrochloric acid.

418. Silver nitrate gives an orange precipitate of silver ferricyanide $\text{Ag}_6[\text{Fe}(\text{CN})_6]_3$. It is insoluble in dilute nitric acid, and dissolves readily in ammonium hydroxide, and in potassium cyanide.

SULPHIDES.

419. The blowpipe tests for sulphides are of little value, except that many of them give the odor of burning sulphur when heated.

Solution Tests.

420. Hydrogen sulphide H_2S is an inflammable gas with a bad odor, and is soluble in water. The water solution has the odor of the gas and turns blue litmus paper red. The gas and its solution in water is decomposed by exposure to the air and contact with oxidizing agents such as chromic, nitric and other oxygen acids, and with the halogens. Ferric chloride also decomposes it. In all these cases sulphur separates.

421. Silver nitrate gives a precipitate of silver sulphide Ag_2S . It is insoluble in dilute acids, alkaline hydroxides and sulphides, but is soluble in potassium cyanide. Boiling nitric acid dissolves it, sulphur separating.

422. Lead acetate gives a precipitate of lead sulphide PbS . It is insoluble in cold dilute acids, alkaline hydroxides and sulphides, and also in potassium cyanide.

423. Sodium nitroprusside added to a solution of a sulphide containing sodium hydroxide, gives a violet red color. This reaction is very delicate.

424. Iron by hydrogen (and free from sulphur) added to a mixture containing sulphides, followed by the addition of dilute hydrochloric acid (1 to 1), gives hydrogen sulphide mixed with hydrogen, and the former may be detected with lead acetate on filter paper held in the gas evolved. See **29**.

SULPHITES.

There are no blowpipe tests for sulphites.

Solution Tests.

425. Hydrogen sulphite H_2SO_3 is the solution of sulphur dioxide in water. It is a colorless fluid having the odor of burning sulphur, reddens litmus paper at first and then bleaches it. Exposure to the air converts this acid into sulphuric acid.

426. Barium chloride gives a precipitate of barium sulphite BaSO_3 . It is soluble in hydrochloric acid.

427. Silver nitrate gives a precipitate of silver sulphite Ag_2SO_3 . It is soluble in nitric acid.

428. Hydrogen sulphide decomposes acid solutions of sulphites, sulphur separating.

429. Hydrogen chloride (hydrochloric acid) decomposes all sulphites, giving sulphur dioxide as a gas, which is detected by its characteristic odor.

430. Zinc and sulphuric acid in a hydrogen generator, together with a sulphite, evolve hydrogen sulphide. The sulphide may be detected with lead acetate on filter paper, which it will turn dark brown or black according to the quantity. This test is very delicate. It should be ascertained that the zinc and sulphuric acid do not give the test without the sulphite.

SULPHATES.

Blowpipe Test.

431. Heated on charcoal with pure sodium carbonate, sulphates are changed into sulphides. If the fused mass is placed on a bright piece of silver and moistened with water, on removing the mass after a few minutes, the metal will be found colored black from formation of silver sulphide.

Solution Tests.

432. Hydrogen sulphate H_2SO_4 is an oily, colorless liquid which destroys or carbonizes organic bodies, and unites with water with the production of much heat.

433. Barium chloride gives a heavy white precipitate of barium sulphate BaSO_4 . It is insoluble in acids, and is one of the most insoluble sulphates known.

434. Lead acetate gives a heavy white precipitate of lead sulphate PbSO_4 . It is almost insoluble in water, still more so in dilute sulphuric acid, and is insoluble in alcohol. It is slightly soluble in dilute nitric acid and dissolves in hot hydrochloric acid. It is soluble in a boiling solution of ammonium acetate or tartrate.

CARBONATES.

The blowpipe tests for carbonates are of little value.

Solution Tests.

435. Hydrogen carbonate H_2CO_3 is the solution of carbon dioxide in water. It has a sweet acid taste and reddens blue litmus paper.

436. All acids decompose carbonates, giving carbon dioxide as a gas. As exceptions to this may be mentioned hydrocyanic acid and hydrogen sulphide. Heating may be necessary in some cases. The carbon dioxide evolved gives a precipitate when passed into lime water.

437. Barium hydroxide gives a precipitate of barium carbonate BaCO_3 . It is soluble in acids with effervescence.

438. Calcium hydroxide gives a precipitate of calcium carbonate CaCO_3 . It is soluble in acids with effervescence.

439. Barium chloride gives a precipitate of barium carbonate BaCO_3 . In solutions containing carbon dioxide not combined with a metal no precipitate is formed.

440. Calcium chloride gives a precipitate of calcium carbonate CaCO_3 . In presence of free carbon dioxide no precipitate is formed.

441. Carbon dioxide or acid carbonates prevent the formation of the red precipitate of ammonium compounds with Nessler's reagent.

ARSENITES.

The blowpipe tests for Arsenic apply to arsenites; see **102 et seq.**

Solution Tests.

442. Hydrogen arsenite H_3AsO_3 is the solution of arsenious oxide in water. This solution is a weak one and turns blue litmus paper red. It is a strong poison.

443. Hydrogen sulphide does not precipitate arsenites until the solutions are made acid, when arsenious sulphide As_2S_3 is formed; see **106.**

444. Ammonium sulphide does not precipitate arsenite solutions; but the addition of hydrochloric acid to a mixture of an arsenite and ammonium sulphide gives a precipitate of arsenious sulphide.

445. Silver nitrate gives a precipitate of silver arsenite; see **107**. Its solution in ammonium hydroxide gives a precipitate of silver on boiling.

446. Copper sulphate gives a precipitate of copper arsenite; see **108**. Its solution in alkaline hydroxides gives cuprous oxide on boiling.

ARSENATES.

The blowpipe tests for Arsenic apply to arsenates. See **102 et seq.**

Solution Tests.

447. Hydrogen arsenate H_3AsO_4 forms deliquescent transparent prisms, soluble in water, giving an acid reaction. It is a strong poison.

448. Hydrogen sulphide does not precipitate alkaline or neutral solutions. See **113**.

449. Ammonium sulphide does not precipitate arsenate solutions; but the addition of hydrochloric acid to a mixture of an arsenate and ammonium sulphide gives a precipitate of arsenic sulphide As_2S_5 . Warming greatly assists the precipitation.

450. Silver nitrate gives a precipitate of reddish-brown silver arsenate Ag_3AsO_4 . See **114**. The solution of silver arsenate in ammonium hydroxide does not precipitate when boiled. Compare **445**.

451. Copper sulphate gives a greenish blue precipitate of copper arsenate $CuHAsO_4$ only on the addition of an alkaline hydroxide, in excess of which the precipitate dissolves to a blue fluid. Boiling the hydroxide solution does not produce cuprous oxide. Compare **446**.

452. Magnesium sulphate, together with ammonium chloride and hydroxide, yields a precipitate of magnesium ammonium arsenate $MgNH_4AsO_4$. See **116**.

453. Molybdic acid in nitric acid gives a fine yellow precipitate on warming if *a few drops only* of an arsenate solution are added to the fluid. This is soluble in ammonium hydroxide, and in this last solution magnesium sulphate with ammonium chloride gives a precipitate of magnesium ammonium arsenate.

PHOSPHATES.

There are no blowpipe tests for phosphates.

Solution Tests.

454. Hydrogen phosphate H_3PO_4 is a white crystalline solid that readily attracts moisture from the air, giving an acid but not a corrosive fluid.

455. Barium chloride gives a white precipitate of barium phosphate BaHPO_4 . It is soluble in nitric and hydrochloric acids, and slightly so in ammonium chloride.

456. Calcium sulphate gives a white precipitate of calcium phosphate CaHPO_4 . It is soluble in acids and also in ammonium chloride.

457. Silver nitrate gives a light yellow precipitate of silver phosphate Ag_3PO_4 . It is readily soluble in nitric acid and in ammonium hydroxide.

458. Ferric chloride added to a solution of a phosphate containing but little free acid and plenty of sodium acetate, gives a yellowish-white precipitate of ferric phosphate FePO_4 . It is soluble in an excess of the ferric chloride, hence care must be taken to avoid this by adding the reagent slowly.

459. Magnesium sulphate gives a white precipitate of magnesium phosphate MgHPO_4 . It is soluble in acids.

460. Magnesium sulphate in presence of ammonium chloride and hydroxide gives a fine crystalline precipitate of ammonium magnesium phosphate MgNH_4PO_4 . It is insoluble in ammonium hydroxide, and only slightly soluble in ammonium chloride. It dissolves readily in acids. The formation of the precipitate is promoted by stirring and shaking the mixture.

461. Molybdic acid in nitric acid gives a fine yellow precipitate if *a few drops only* of a phosphate solution are added to the

fluid, and the mixture is very gently warmed. It is insoluble in dilute acids only when molybdic acid is also present. It is soluble in ammonium hydroxide, from which solution magnesium sulphate with ammonium chloride precipitate ammonium magnesium phosphate.

N. B.—Compare this last test with **369**.

BORATES.

Blowpipe Test.

462. Borates mixed into a paste with sulphuric acid, and placed in a loop of platinum wire which has been moistened with glycerin, give a fine grass-green flame when heated in the blowpipe. This color is around the margin of the flame, and only lasts for a moment.

463. Borates made into a paste with water, mixed with potassium acid sulphate and calcium fluoride (5 of the first and 1 of the second), and heated before the blowpipe, give a green color, due to boron fluoride.

Solution Tests.

464. Hydrogen borate (boracic acid) H_3BO_3 , is a white solid soluble in water and alcohol. The solutions turn blue litmus paper red. If the solutions are evaporated, the bulk of the acid is volatilized.

465. Alcohol, mixed with borates, made acid with sulphuric acid and then ignited, gives a green flame. Use plenty of acid and allow the action to go on for some time.

466. Barium chloride, in moderately strong solutions of borates, gives a precipitate of barium borate, BaB_2O_4 . It is soluble in acids and ammonium salts.

467. Silver nitrate, in strong solutions of borates, gives a precipitate of silver borate, $AgBO_2$. This is yellowish, due to some brown silver oxide mixed with it. In dilute solutions the precipitate is brown silver oxide. All these precipitates are soluble in acids and ammonium salts.

468. Turmeric paper, moistened with solution of a borate that is *just* acid with hydrochloric acid, and dried at $100^\circ C.$, shows a

peculiar red color that is very characteristic. Great care must be taken not to have too much acid present, as strong hydrochloric acid alone may produce a similar tint.

CHROMATES.

Blowpipe Test.

469. Borax in a bead gives an emerald-green glass with chromates.

Solution Tests.

470. Hydrogen chromate, H_2CrO_4 , is the solution of chromium trioxide CrO_3 in water. It gives a bright yellow fluid which turns blue litmus paper red. The color of the solution is very marked, even if very dilute.

471. All chromates are colored red or yellow. It is therefore useless to test a colorless solution for chromates.

472. Hydrogen sulphide in presence of an acid converts the chromates in a solution into chromium salts, changing the color of the fluid from red or yellow to green. As a result of this change, sulphur separates and the solution becomes milky. Heat assists the action. This change must be remembered in the separation of the metals, since chromium may be found in the third group which came from chromates in the substance, and not from chromium salts.

473. Chromates may also be changed to chromium salts in acid solutions by other reducing agents, such as sulphur dioxide, alcohol, tartaric, oxalic and other organic acids, or by zinc.

474. Ammonium sulphide changes chromates to chromium salts and gives a precipitate of chromium hydroxide. Boiling completes the precipitation.

475. Barium chloride gives a yellowish-white precipitate of barium chromate, BaCrO_4 . It is soluble in dilute hydrochloric and nitric acids.

476. Silver nitrate gives a purplish-red precipitate of silver chromate Ag_2CrO_4 . It is soluble in nitric acid and ammonium hydroxide. In slightly acid solutions silver dichromate $\text{Ag}_2\text{Cr}_2\text{O}_7$ is formed.

477. Lead acetate gives a yellow precipitate of lead chromate PbCrO_4 . It is insoluble in water and in acetic acid. It is soluble in sodium or potassium hydroxide, and slightly in dilute nitric acid.

FLUORIDES.

The blowpipe tests are of little value.

Solution Tests.

478. Hydrogen fluoride HF is a colorless liquid which fumes in the air like hydrochloric acid. It is kept in rubber or lead bottles because it has the property of dissolving glass.

479. Barium chloride gives a precipitate of barium fluoride BaF_2 . It is white and bulky and insoluble in water. It is soluble in hydrochloric and nitric acids, and these solutions are not precipitated by ammonium hydroxide, as the barium fluoride is soluble in ammonium salts.

480. Calcium chloride gives a precipitate of calcium fluoride CaF_2 . It is nearly transparent, and the solution may appear clear and yet have much precipitate in it. It is insoluble in water, and in alkaline liquids. Ammonium hydroxide promotes its precipitation.

481. Sulphuric acid added to a dry fluoride causes the evolution of hydrogen fluoride gas, which etches glass. This test is best made in a lead or platinum vessel covered with glass coated with wax, into which some writing is cut to expose a small portion of the glass surface. After exposure to the fumes of the gas, on removing the wax, the etching of the glass can be readily seen, where the wax was removed (see also **357**).

SILICATES.

Blowpipe Tests.

482. Heated in a bead of sodium metaphosphate, silicates give an insoluble skeleton of silica. Sodium metaphosphate is made by fusing sodium ammonium phosphate.

483. Fused with a mixture of sodium and potassium carbonates, silicates are decomposed, giving sodium and potassium silicates

soluble in water, while the metals previously in combination remain as insoluble compounds (except aluminium).

Solution Tests.

484. Acids decompose solutions of silicates, giving hydrogen silicate which in dilute solution may remain dissolved, or may separate as a gelatinous precipitate. If the acid mixture is evaporated to dryness and dried at a temperature of 150° C., then treated with acid again, the metals will pass into solution, and insoluble silica will remain.

485. Ammonium chloride precipitates hydrogen silicate in solutions of silicates if they are not too dilute.

ACETATES.

Blowpipe Test.

486. Heat decomposes acetates, some yielding a carbonized residue, others giving off acetone, while a carbonate remains in the residue. Ammonium acetate is completely volatilized by heat.

Solution Tests.

487. Hydrogen acetate $\text{HC}_2\text{H}_3\text{O}_2$ forms transparent crystalline plates which are readily soluble in water, giving a strongly acid liquid. It is also soluble in alcohol. The melted crystals give a liquid boiling at 119° C. Its vapor is inflammable.

488. Ferric chloride gives a precipitate of basic ferric acetate on boiling, but only in solutions which are neutral or contain very little acetic acid. If the ferric chloride is added to an acetate containing a little acetic acid, the fluid acquires a deep red color which, on boiling, gives basic ferric acetate. The red color becomes yellow on adding hydrochloric acid.

489. Silver nitrate in neutral solutions of acetates gives a precipitate of white crystalline silver acetate $\text{AgC}_2\text{H}_3\text{O}_2$, which is slightly soluble in cold water, but dissolves in hot water, from which it crystallizes on cooling. It is soluble in ammonium hydroxide.

490. Mercurous nitrate gives a white scaly precipitate of mercurous acetate $\text{Hg}_2(\text{C}_2\text{H}_3\text{O}_2)_2$. It is slightly soluble in cold water

and in acetic acid, and is also slightly soluble in an excess of the precipitant. It is soluble in hot water, from which it crystallizes on cooling.

491. Alcohol and sulphuric acid added to an acetate produce acetic ether, having a very characteristic odor. Care must be taken not to have too much alcohol, and the fluid should be only just warm at the first; the odor is best noted on cooling and shaking the mixture.

OXALATES.

492. All oxalates are decomposed when heated to redness.

Solution Tests.

493. Hydrogen oxalate $\text{H}_2\text{C}_2\text{O}_4$ is a white powder soluble in water and alcohol. When heated, the acid partly volatilizes and is partly decomposed.

494. Barium chloride gives a white precipitate of barium oxalate BaC_2O_4 . It is slightly soluble in water, but dissolves more readily in ammonium chloride, also in acetic and oxalic acids. It is readily soluble in nitric and hydrochloric acids, from which ammonium hydroxide reprecipitates it.

495. Calcium chloride gives a white precipitate of calcium oxalate CaC_2O_4 . It is insoluble in water, and almost so in acetic and oxalic acids. It is soluble in nitric and hydrochloric acids. In dilute solutions the precipitate forms only after some time.

496. Calcium hydroxide gives the same precipitate as that obtained with calcium chloride.

497. Calcium sulphate also gives the same precipitate.

498. Silver nitrate gives a white precipitate of silver oxalate $\text{Ag}_2\text{C}_2\text{O}_4$. It is very slightly soluble in water, dissolves more readily in dilute nitric acid, and is readily soluble in hot nitric acid and ammonium hydroxide.

499. Manganese dioxide mixed with an oxalate and moistened with water evolves carbon dioxide as a gas, on adding a few drops of sulphuric acid to the mixture. The gas may be detected by making the experiment in a watch glass, and holding over the mix-

ture another watch glass moistened with calcium hydroxide. A clouding of the upper glass indicates carbon dioxide. Care must be taken that the manganese dioxide used does not contain carbonate.

TARTRATES.

Blowpipe Test.

500. Heated on charcoal, tartrates carbonize and emit a very characteristic odor, resembling burning sugar or burning grapes.

Solution Tests.

501. Hydrogen tartrate $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ forms colorless crystals of a lemon-like taste, which are soluble in water and alcohol.

502. Potassium acetate and other potassium salts, in presence of acetic acid, give a white crystalline precipitate of potassium acid tartrate $\text{KHC}_4\text{H}_4\text{O}_6$. It is soluble in alkaline hydroxides and in acids, but tartaric and acetic acids do not increase its solubility in water. Stirring and shaking assist the formation of the precipitate. If borates are present, potassium fluoride, and not the acetate, must be used to make the test, for borates form a soluble compound with potassium tartrate in presence of acetic acid.

503. Calcium chloride, added in excess to neutral solutions of tartrates produces a white precipitate of calcium tartrate $\text{CaC}_4\text{H}_4\text{O}_6$. Stirring and shaking assist the precipitation. It is soluble in alkaline hydroxides. Ammonium salts retard the formation of the precipitate.

504. Calcium hydroxide added in excess to solutions of tartrates gives a precipitate of calcium tartrate.

505. Lead acetate gives a precipitate of lead tartrate $\text{PbC}_4\text{H}_4\text{O}_6$, which is soluble in nitric acid and in ammonium hydroxide.

506. Silver nitrate added to a neutral solution of a tartrate gives a white precipitate of silver tartrate $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$. On adding ammonium hydroxide to the fluid containing the precipitate until the latter is almost (but not quite) dissolved, and then boiling the mixture, a mirror of metallic silver will be deposited on the tube.

CITRATES.

Blowpipe Test.

507. Heated on charcoal, citrates carbonize and give an odor that is of an acrid character and differs from the odor of tartrates.

Solution Tests.

508. Hydrogen citrate $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ forms colorless, transparent crystals of a purely acid taste, which are soluble in water and alcohol.

509. Calcium chloride gives no precipitate with citric acid; but if it is added to a neutral citrate solution in excess, white calcium citrate $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ is formed. This is soluble in alkaline citrates and in ammonium chloride. From the last solution it is again precipitated on boiling, unless too much chloride is present. A solution of a citrate mixed with calcium chloride in excess, and then with ammonium hydroxide in excess, gives no precipitate until it is boiled, when calcium citrate is formed.

510. Calcium hydroxide added in excess gives no precipitate in the cold, but, on boiling, calcium citrate is formed, which dissolves again on cooling.

511. Lead acetate gives a white precipitate of lead citrate $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2$, which is soluble in ammonium hydroxide.

512. Silver nitrate gives, in neutral solutions of citrates, a white precipitate of silver citrate $\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$, which, when boiled with a little water, is decomposed, depositing silver. Silver citrate treated like silver tartrate in **506** gives no mirror.

CHAPTER XIV.

PREPARATION OF SOLUTIONS.

513. The character of the solution used to make the analysis will often determine the presence or absence of certain metals or acid-radicals. For example, lead and sulphuric acid or barium and sulphuric acid cannot exist in any water solution, since both these combinations are insoluble in water. It is therefore quite necessary to ascertain if the solution is acid, alkaline or neutral when starting an analysis. The beginner should acquire the habit of testing a fluid given to him in order to determine this point at once.

514. Another important point to be remembered also is the fact that in acid solutions too much acid may interfere with the use of hydrogen sulphide, and if the solution is acid with nitric acid this will require much more dilution than in the case of hydrochloric acid. Here again we may get an indication of the presence of two metals in a solution from its behavior on dilution. If the addition of water to an acid solution gives a milky precipitate, the presence of bismuth or antimony may be suspected.

515. When the substance to be analyzed is a solid, it is treated with various liquids to ascertain which is the best solvent for it.

As water is the best solvent as far as the method of analysis is concerned, this is always used first. Having reduced the solid to a fine powder, shake it with some cold water; if this dissolves the whole of it, the solution may be used for the analysis at once. If cold water does not give a solution, boil the powdered solid with water; and if this dissolves it, use the fluid for analysis. But in both these cases take care that there is enough material in solution to serve the purpose of the scheme of separation of the metals. Judge of this from the reduction of volume of the substance.

516. Should the solid not dissolve in water, or only partially dissolve, place the tube containing the experiment on one side, and then try to dissolve the substance in hydrochloric acid; first,

in dilute acid (1 in 3) cold and boiling, and then in strong acid cold and boiling. Take care not to use any more acid than is absolutely necessary. If the strong acid has been used and gives a solution, dilute the fluid with ten times its volume of water, and note if a precipitate is produced; in this case some other solvent must be used.

517. If hydrochloric acid fails to produce a satisfactory solution, proceed with nitric acid, cold and hot, and in a like manner as with the former acid.

518. Should nitric acid refuse to give a solution that will bear dilution with at least fifteen volumes of water, make aqua regia (1 of nitric acid and 2 of hydrochloric acid), and see if this will give a solution that will bear dilution, either from the cold or hot fluid. It must be remembered that diluting the aqua regia is not admissible until after it has dissolved the substance; it is not used in a dilute state to make the substance dissolve. Furthermore, in heating aqua regia it is decomposed on boiling, and then loses its value as a solvent; warm it gently to get the best results.

All these tests of solubility must be made on separate portions of the finely powdered substance.

519. If hydrochloric acid or aqua regia give complete solution which will bear dilution, it is evident that metals of the first group are absent (except perhaps traces of lead), since these give insoluble chlorides.

520. Substances which are not dissolved by any of the acids mentioned, or which are only partially dissolved, are best treated as insoluble. To obtain solutions of insoluble substances proceed as follows:

Boil a portion of the finely powdered substance with several fresh quantities of ammonium acetate, and filter. Put the solutions thus obtained on one side (see **522**).

Wash the material insoluble in ammonium acetate, and warm it with solution of potassium cyanide, using several fresh portions, and filter. Put these solutions on one side (see **523**).

521. The material insoluble in potassium cyanide is now washed and dried. Fuse the dry substance insoluble in potassium cyanide with two parts each of a mixture of dry potassium and sodium car-

bonates and one part of potassium nitrate. When the mixture is melted, allow it to cool, and treat it with water in several portions, boiling the last. The insoluble matter contains the metals (except aluminium) with some silicates, and the solution contains the acid radical and aluminium. Dissolve the insoluble matter from the fusion in hydrochloric acid, and proceed with this solution as in the ordinary method of analysis. Proceed to test the water solution from the fusion for acids as in **343** and **359**.

522. The solution in ammonium acetate may contain lead chloride or sulphate. To a portion of it add nitric acid in excess and then silver nitrate; a white precipitate soluble in ammonium hydroxide indicates *chlorides*. To another portion add hydrochloric acid in excess, filter if necessary, and then add barium chloride; a white precipitate insoluble in hydrochloric acid indicates *sulphates*. To a third portion add sulphuric acid in excess; a white precipitate indicates *lead*.

523. The solution in potassium cyanide may contain silver chloride, and a little sulphate from barium sulphate (if present) decomposed by potassium carbonate in the potassium cyanide used. To one portion of this fluid add ammonium sulphide; a black precipitate indicates *silver*. Filter out this precipitate and dissolve it in nitric acid, dilute the solution, and add hydrochloric acid to prove that it contains silver. If silver is present, precipitate another portion of the cyanide solution with ammonium sulphide in excess, to remove all the silver, mix the filtrate with sodium carbonate and evaporate to dryness. The dry residue will contain the *acids*, and may be tested in the ordinary way. See **343** and **359**. Remember there are only a few insoluble silver compounds.

CHAPTER XV.

SPECIAL METHODS.

MODIFICATION OF THE PROCESS FOR GROUP III. WHEN PHOSPHATES AND OXALATES ARE PRESENT.

524. If a substance is insoluble in water, the presence of phosphates or oxalates may be expected. In this case the process for the separation of Group III. must be modified. To ascertain if this is necessary proceed as follows :

Test for phosphates in the original material by dissolving in nitric acid and adding a few drops of this solution to molybdic solution, see **461**.

Mix some of the original material (solid or liquid) with sulphuric acid and evaporate nearly to dryness ; a black carbonaceous residue indicates organic matter.

If phosphates or organic matter or both have been found, the process for Group III. is modified as follows :

525. After filtering out any nickel or cobalt sulphides which are left undissolved by dilute hydrochloric acid in the ordinary process, boil the filtrate in a dish to expel hydrogen sulphide. To this solution add nitric acid to oxidize the iron if any be present, and also to destroy organic matter. Add the acid until the solution in the dish shows no change after boiling some minutes, using small quantities at a time.

Put a few drops of this last solution into a test-tube, add a few drops of hydrochloric acid and boil nearly to dryness. Dilute the fluid with a little water and add potassium sulphocyanide ; a red color indicates the presence of iron (Group III.).

Having proved the presence or absence of iron (Group III.), proceed with the rest of the solution, as follows :

526. To the solution add ammonium hydroxide slowly until a small precipitate is formed ; now add hydrochloric acid drop by drop until the solution clears up on shaking. To this fluid add

ammonium acetate (ammonium hydroxide with acetic acid in slight excess) equal to one-fourth of the volume of the fluid; now add ferric chloride slowly until it will not give any more precipitate after shaking well and allowing the precipitate to settle, testing the clear solution above. This will precipitate all the phosphate present as ferric phosphate. Any organic matter present will have been destroyed by the evaporation with nitric acid **525**; hence if no precipitate is obtained with ferric chloride on the addition of the first drop, it is useless to add any more, and the fluid is treated as follows:

527. To the filtrate from the ferric phosphate, or the fluid that it will not precipitate, add ammonium hydroxide in excess, then ammonium sulphide in excess and filter. The precipitate will contain the metals of Group III., except nickel and cobalt; wash it and proceed as in the ordinary method of separation. The filtrate from the ammonium sulphide precipitate is added to the first filtrate from the precipitation of Group III., and the mixture now contains the metals of Group IV. to be treated in the regular manner.

SEPARATION OF ARSENIC, ANTIMONY AND TIN BY FUSION METHOD.

528. The dried sulphides from the ammonium sulphide solution of Group II. are ground with a mixture of one part of sodium carbonate and three parts of sodium nitrate. This mixture is fused at as low a temperature as possible in a porcelain crucible. The fused mass when cold is treated with cold water, which dissolves the arsenic as sodium arsenate, while the tin and antimony are in the insoluble matter. This latter is washed with dilute alcohol (one of alcohol and three of water) put into a dish with zinc and hydrochloric acid and tested in the ordinary manner. The solution of the fusion is made acid with nitric acid and silver nitrate added. If a precipitate is formed, filter it out, and to the filtrate add dilute ammonium hydroxide (one of solution with ten of water) inclining the tube so that the fluid floats on the filtrate. At the junction of the two liquids a reddish-brown precipitate of silver arsenate is formed if arsenic is present.

SEPARATION OF NICKEL AND COBALT.

529. After dissolving the two sulphides obtained in Group

III. in *aqua regia*, boil off nearly all the acid and dilute with a little water. To this slightly acid solution add potassium cyanide solution (1 in 5) until the precipitate first formed is just redissolved. If the solution, after adding the cyanide, becomes alkaline, add a drop or two of hydrochloric acid—it must be acid. Now boil the mixture and if a precipitate is formed add more cyanide and acid. Boil the solution again, and add to it, while boiling, sodium hypochlorite solution until it is alkaline, boiling continuously. The precipitate is nickel sesquioxide and the solution contains the cobalt. Test each in a borax bead.

SEPARATION OF BARIUM FROM STRONTIUM AND CALCIUM.

530. Instead of following the method given in **252** the process given below is very convenient :

The carbonates of barium, strontium and calcium obtained in **14** are carefully washed as usual and then dissolved in acetic acid, using as small a quantity as possible to obtain complete solution. To the fluid thus obtained add potassium bichromate, a few drops at a time. If no precipitate is obtained, barium is absent. Should a yellow precipitate form, add more bichromate, until it no longer produces a precipitate. Filter out the barium chromate (which indicates the presence of barium) and treat the filtrate according to **256** to separate strontium from calcium. Mix the fluid with its own volume of alcohol before proceeding.

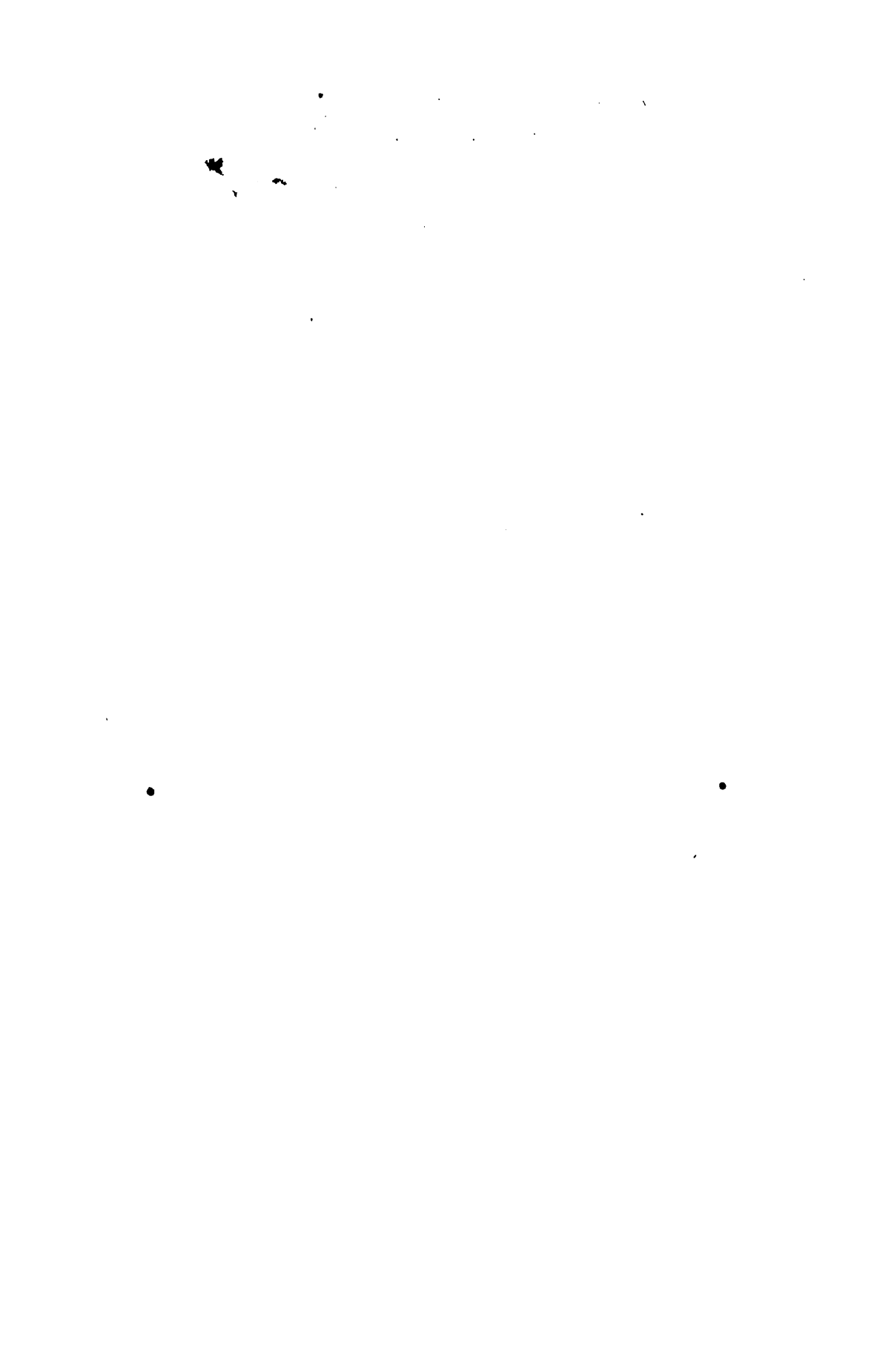
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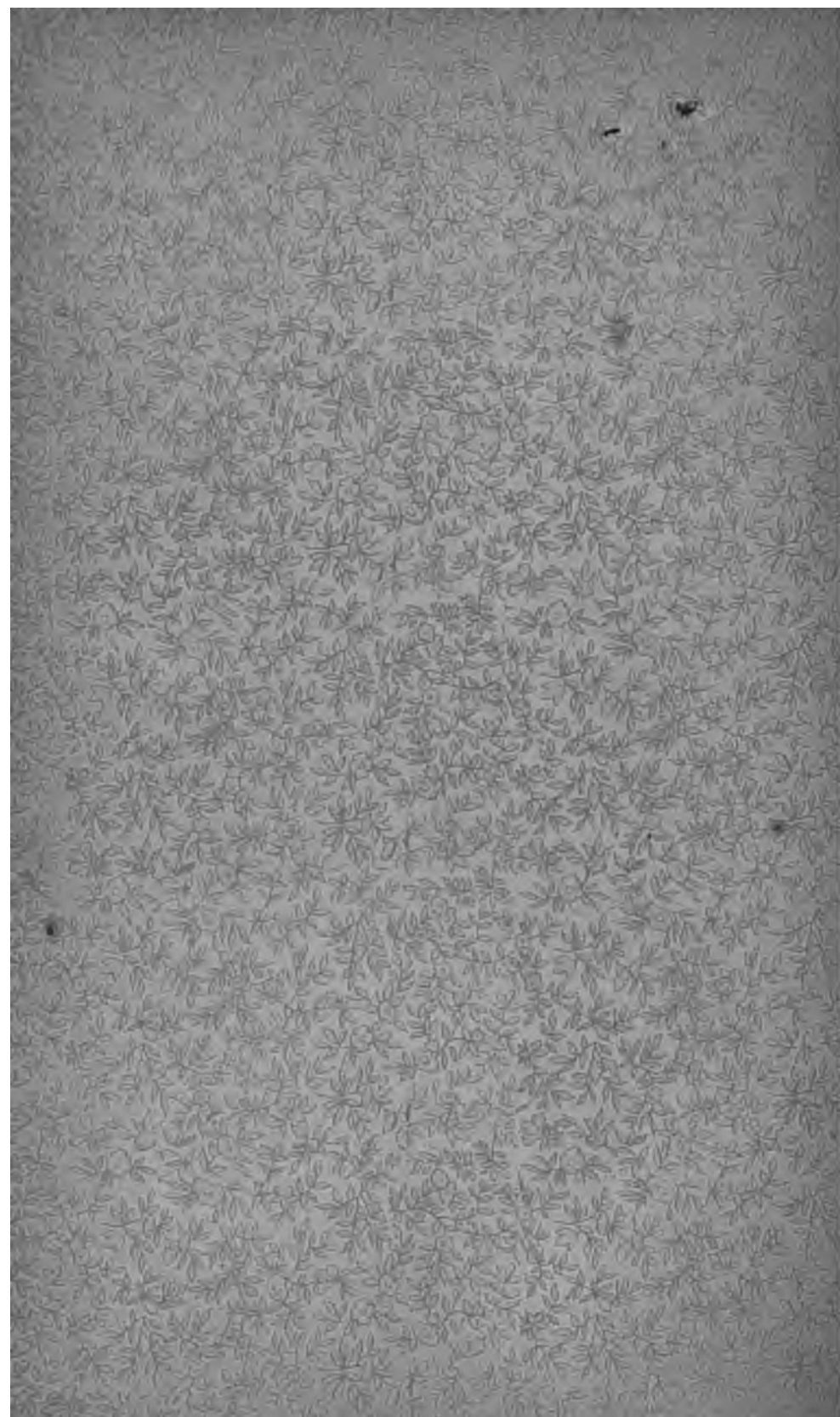
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